

# MOLE CONCEPT

## 1. MOLE

A mole is the amount of substance that contains as many species [Atoms, molecules, ions or other particles] as there are atoms in exactly 12 gm of C-12.

$$1 \text{ mole} = 6.022 \times 10^{23} \text{ species}$$

### 2.1 Atomic mass

Atomic mass of an element can be defined as the number which indicates how many times the mass of one atom of the element is heavier in comparison to  $\frac{1}{12}$ th part of the mass of one atom of Carbon-12.

$$\text{Atomic mass} = \frac{[\text{Mass of an atom of the element}]}{\frac{1}{12} \times [\text{Mass of an atom of carbon - 12}]} = \frac{\text{Mass of an atom in amu}}{1 \text{ amu}}$$

### 2.2 Atomic mass unit (amu) or Unified mass (u)

The quantity  $[\frac{1}{12} \times \text{mass of an atom of C-12}]$  is known as atomic mass unit.

The actual mass of one atom of C-12 =  $1.9924 \times 10^{-26} \text{ kg}$

$$\therefore 1 \text{ amu} = \frac{1.9924 \times 10^{-26}}{12} \text{ kg}$$

$$= 1.66 \times 10^{-27} \text{ kg} = 1.66 \times 10^{-24} \text{ gm} = \frac{1}{N_A} \text{ gm}$$

### 2.3 Gram atomic mass

The gram atomic mass can be defined as the mass of 1 mole atoms of an element.

$$\text{e.g., Mass of one oxygen atom} = 16 \text{ amu} = \frac{16}{N_A} \text{ gm.}$$

$$\text{Mass of } N_A \text{ oxygen atom} = \frac{16}{N_A} \cdot N_A = 16 \text{ gram}$$



**Illustration**

- (a) What is the mass of one atom of Cl?      (b) What is the atomic mass of Cl?  
 (c) What is the gram atomic mass of Cl?

**Sol.** (a) Mass of one atom of Cl = 35.5 amu.

$$(b) \text{ Atomic mass of Cl} = \frac{\text{Mass of an atom in amu}}{1 \text{ amu}} = \frac{35.5 \text{ amu}}{1 \text{ amu}} = 35.5$$

$$(c) \text{ Gram atomic mass of Cl} = [\text{Mass of 1 Cl atom} \times N_A]$$

$$= 35.5 \text{ amu} \times N_A = \frac{35.5}{N_A} \times N_A \text{ gram} = 35.5 \text{ gram}$$

**Exercise**

- (a) What is the mass of one atom of S?  
 (b) What is the atomic mass of S?  
 (c) What is the gram atomic mass of S?

**Ans.** (a) 32 amu, (b) 32, (c) 32 gram

**3.1 Molecular mass**

Molecular mass is the number which indicates how many times one molecule of a substance is heavier in comparison to  $\frac{1}{12}$ th of the mass of one atom of C-12.

$$\begin{aligned} \text{Molecular mass} &= \frac{\text{Mass of one molecule of the substance (in amu)}}{\frac{1}{12} \times [\text{Mass of an atom of C - 12}]} \\ &= \frac{\text{Mass of one molecule of the substance (in amu)}}{1 \text{ amu}} \end{aligned}$$

**3.2 Gram Molecular mass**

Gram molecular mass can be defined as the mass of 1 mole of molecules.

$$\text{e.g., Mass of one molecule of O}_2 = 32 \text{ amu} = \frac{32}{N_A} \text{ gram.}$$

$$\text{Mass of } N_A \text{ molecules of O}_2 = \frac{32}{N_A} \times N_A \text{ gm} = 32 \text{ gm}$$

**Illustration**

(a) What is the mass of one molecule of  $\text{HNO}_3$ ?

(b) What is the molecular mass of  $\text{HNO}_3$ ?

(c) What is the gram molecular mass of  $\text{HNO}_3$ ?

**Sol.** (a) Mass of one molecule of  $\text{HNO}_3 = (1 + 14 + 3 \times 16) \text{ amu} = 63 \text{ amu}$ .

(b) Molecular mass of  $\text{HNO}_3 = \frac{63 \text{ amu}}{1 \text{ amu}} = 63$

(c) Gram molecular mass of  $\text{HNO}_3 = \text{Mass of 1-molecule of } \text{HNO}_3 \times N_A$

$$= 63 \text{ amu} \times N_A = \frac{63}{N_A} \text{ gm} \times N_A = 63 \text{ gram}$$

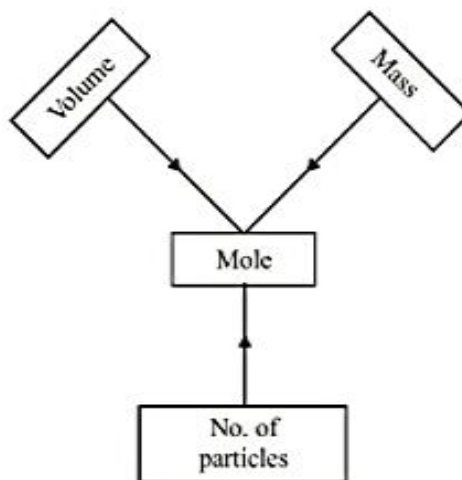
**Exercise**

(a) What is the mass of one molecule of  $\text{H}_2\text{SO}_4$ ?

(b) What is the molecular mass of  $\text{H}_2\text{SO}_4$ ?

(c) What is the gram molecular mass of  $\text{H}_2\text{SO}_4$ ?

**Ans.** (a) 98 amu (b) 98 (c) 98 gram

**4. METHODS TO CALCULATE MOLES****4.1 From number of particles :**

$$\text{No. of mole} = \frac{\text{Given no. of Particles [atoms/molecules/ ions]}}{N_A}$$

**Illustration**

A piece of Cu contains  $6.022 \times 10^{24}$  atoms. How many mole of Cu atoms does it contain?

**Sol.** No. of mole =  $\frac{6.022 \times 10^{24}}{N_A} = \frac{6.022 \times 10^{24}}{6.022 \times 10^{23}} = 10 \text{ mole}$

**Exercise**

5 mole of  $\text{CO}_2$  are present in a gaseous sample. How many molecules of  $\text{CO}_2$  are present in the sample?

**Ans.**  $5 N_A$

**4.2 From given Mass :**

(a) For atoms : No. of mole =  $\frac{\text{Given mass of the substance(gm)}}{\text{Gram atomic mass}} = \text{No. of g-atoms}$

(b) For molecules : No. of mole =  $\frac{\text{Given mass of the substance(gm)}}{\text{Gram molecular mass}} = \text{No. of g-molecules}$

**Illustration**

What will be the mass of 5 mole of  $\text{SO}_2$ ?

**Ans.** Molecular mass of  $\text{SO}_2 = 64 \text{ gm}$

$$5 = \frac{\text{mass (gm)}}{64}$$

$$\therefore \text{mass} = 320 \text{ gm}$$

**Exercise**

(a) How many mole of O atoms are present in 88 gm  $\text{CO}_2$ ?

(b) What will be the mass of 10 mole of  $\text{H}_3\text{PO}_4$ ?

**Ans.** (a) 4 mole (b) 980 gm

**4.3 From the given volume of a gas :**

$$n = \frac{\text{volume of gas at 1 bar pressure and } 273 \text{ K (in litre)}}{22.7}$$

**S.T.P.:** 1 bar pressure and 273 K.

$$n = \frac{\text{volume of gas at 1 atm and } 273 \text{ K (in litre)}}{22.4}$$

*Note: According to old IUPAC agreement, STP condition was 1 atm pressure and 273 K temperature but according to new agreement it is 1 bar pressure and 273K temperature. Although many books are still using the condition of 1 atm and 273K for STP.*

If volume is given under any other condition of temperature and pressure, then use the ideal gas equation to find the no. of moles.

$$\text{No. of mole}(n) = \frac{PV}{RT}$$

#### Units of Pressure :

$$1 \text{ atm} = 76 \text{ cm Hg} = 760 \text{ torr} = 1.01325 \text{ bar} = 1.01325 \times 10^5 \text{ pa.}$$

#### Units of temperature :

$$K = ^\circ C + 273$$

#### Value of R :

$$R = 0.0821 \text{ litre-atm/mole.K}$$

$$= 8.314 \text{ J/mole.K} = 1.987 \approx 2 \text{ cal/mole.K}$$

#### Units of volume :

$$1 \text{ dm}^3 = 10^3 \text{ cm}^3 = 1 \text{ litre} = 10^{-3} \text{ m}^3 = 10^3 \text{ ml}$$

$$1 \text{ m}^3 = 10^3 \text{ litre}$$

#### Illustration

A sample of He gas occupies 5.6 litre volume at 1 atm and 273 K. How many mole of He are present in the sample?

**Sol.**  $\text{No. of mole} = \frac{5.6}{22.4} = 0.25$

#### Exercise

How much volume will be occupied by 2 mole  $\text{CO}_2$  gas at STP?

**Ans.** 45.4 L

**Note :** We can use the following relationship as per requirement of question.

$$\text{No. of mole} = \frac{\text{No. of particle}}{N_A} = \frac{\text{mass (gm)}}{[\text{gm at. or mol. mass}]}$$

$$= \frac{V(\ell) \text{ occupied by a Gas at STP}}{22.7} = \frac{V(\ell) \text{ occupied by a Gas at 1 atm and 273K}}{22.4}$$

**Illustration**

How many molecules of  $O_2$  are present in 5.6 litres of  $O_2$  at 1 atm and 273 K?

**Sol.** 
$$\frac{\text{No. of molecules}}{N_A} = \frac{V(\ell) \text{ at 1 atm and 273 K}}{22.4}$$

$$\frac{\text{No. of molecules}}{N_A} = \frac{5.6}{22.4} = \frac{1}{4} \Rightarrow \text{No. of molecule} = \frac{N_A}{4} = 1.505 \times 10^{23}$$

**Exercise**

How many molecules of water are present in 9 gram of water?

**Ans.**  $3.011 \times 10^{23}$

**5. LAWS OF CHEMICAL COMBINATION****5.1 Law of conservation of mass (Lavoisier – 1774) :**

In any physical or chemical change, mass can neither be created nor be destroyed.

**It means :**

Total mass of the reactants = total mass of the products.

This relationship holds good when reactants are completely converted into products.

In case the reacting material are not completely consumed the relationship will be –

Total mass of the reactants = Total mass of the products + mass of unreacted reactants

**Limitation :** In nuclear reactions, some mass of reactant is converted into energy, so mass of reactant is always less than that of product.

**Illustrations**

1.7 gram of silver nitrate dissolved in 100 gram of water is taken. 0.585 gram of sodium chloride dissolved in 100 gram of water is added to it and chemical reaction occurs. 1.435 gm of  $AgCl$  and 0.85 gm  $NaNO_3$  are formed. Show that these results illustrate the law of conservation of mass.

**Sol.** Total mass before chemical change = mass of  $AgNO_3$  + Mass of  $NaCl$  + Mass of water  
 $= 1.70 + 0.585 + 200 = 202.285 \text{ gram}$

Total mass after the chemical reaction = mass of  $AgCl$  + Mass of  $NaNO_3$  + Mass of water  
 $= 1.435 + 0.85 + 200 = 202.285 \text{ gram}$

Thus in the given reaction

Total mass of reactants = Total mass of the products.

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**Exercise**


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If 6.3 gram of  $\text{NaHCO}_3$  are added to 15 gram  $\text{CH}_3\text{COOH}$  solution. The residue is found to weigh 18 gram. What is the mass of  $\text{CO}_2$  released in this reaction?

**Ans.** 3.3 gram

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**5.2 Law of constant composition : [Proust 1799]**

A chemical compound always contains the same element combined together in fixed proportion by mass.

**Limitations :** In case of isotopes, ratio is not fixed

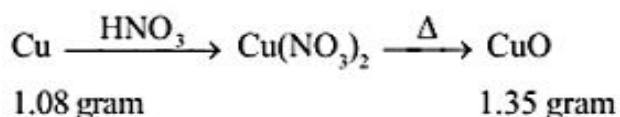
e.g.	$^{12}\text{CO}_2$	$^{14}\text{CO}_2$
	12 : 32	14 : 32
	3 : 8	7 : 16

**Illustration**


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1.08 gram of Cu wire was allowed to react with nitric acid. The resulting solution was dried and ignited when 1.35 gram of copper oxide was obtained. In another experiment 2.3 gram of copper oxide was heated in presence of Hydrogen yielding 1.84 gram of copper. Show that the above data are in accordance with law of constant composition?

**Sol. Case-I**



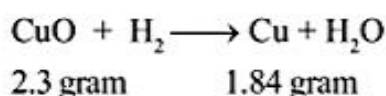
1.35 gram CuO contains  $\longrightarrow$  1.08 gram Cu.

$$100 \text{ gram CuO contains } \longrightarrow \frac{1.08}{1.35} \times 100 = 80 \text{ gram Cu}$$

% Cu in CuO = 80%

% O in CuO = 20%

**Case-II**



2.30 gram CuO contains  $\longrightarrow$  1.84 gram Cu.

$$100 \text{ gram CuO contains } \longrightarrow \frac{1.84 \times 100}{2.30} = 80 \text{ gram Cu}$$

% Cu in CuO = 80%

% O in CuO = 20%

Both sample have the same composition & hence the data are in accordance with law of constant composition.

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**Exercise**

7.95 gram of cupric oxide was reduced by heating in a current of hydrogen and the weight of copper that remained was 6.35 gram. In another experiment, 19.05 gram of Cu was dissolved in the nitric acid and the resulting copper nitrate is converted into cupric oxide by ignition. The weight of cupric oxide formed was 23.85 gram. Show that these results illustrate the law of constant composition.

**5.3 Law of multiple proportion : [Dalton 1806]**

When two elements combine to form two or more compounds, the different masses of one element which combine with a fixed mass of the other element, bear a simple ratio to one another.

**Illustration**

Two compounds each containing only tin and oxygen had the following composition.

	Mass % of Tin	Mass % of oxygen
Compound A	78.77	21.23
Compound B	88.12	11.88

Show that these data illustrate the law of multiple proportion?

**Sol.**

**In compound A**

21.23 parts of oxygen combine with 78.77 parts of tin.

1 part of oxygen combine with  $\frac{78.77}{21.23} = 3.7$  parts of Sn.

**In compound B**

11.88 parts of oxygen combine with 88.12 parts of tin.

1 part of oxygen combined with  $\frac{88.12}{11.88} = 7.4$  parts of tin.

Thus the mass of Tin in compound A and B which combine with a fixed mass of oxygen are in the ratio 3.7 : 7.4 or 1 : 2. This is a simple ratio. Hence the data illustrate the law of multiple proportion.

**Exercise**

Carbon and oxygen are known to form two compounds. The carbon content in one of these is 42.9% while in the other it is 27.3%. Show that these data are in agreement with the law of multiple proportion.

**5.4 Law of reciprocal proportion : [Richter 1794]**

When two different elements combine with the same mass of a third element, the ratio in which they do so will be same or simple multiple if both directly combined with each other.

**Illustration**

The % composition of  $\text{NH}_3$ ,  $\text{H}_2\text{O}$  and  $\text{N}_2\text{O}_3$  is as given below :

$\text{NH}_3 \longrightarrow 82.35\% \text{ N and } 17.65\% \text{ H.}$

$\text{H}_2\text{O} \longrightarrow 88.9\% \text{ O and } 11.1\% \text{ H}$

$\text{N}_2\text{O}_3 \longrightarrow 63.15\% \text{ O and } 36.85\% \text{ N}$

On the basis of above data prove the law of reciprocal proportion?

**Sol.** (i) For  $\text{NH}_3$  1-part of hydrogen reacts with  $= \frac{82.35}{17.65} = 4.67$  part N.

(ii) For  $\text{H}_2\text{O}$  1-part of hydrogen reacts with  $= \frac{88.90}{11.10} = 8.01$  part O.

Thus the ratio  $\text{N} : \text{O} = 4.67 : 8.01 = 1 : 1.71$

(iii) For  $\text{N}_2\text{O}_3$  : N and O reacts with each other  $\text{N} : \text{O} = 36.85 : 63.15 = 1 : 1.71$

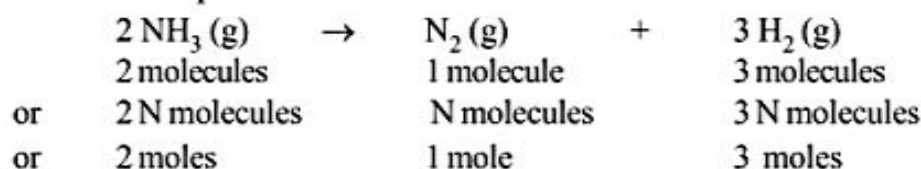
Because the two ratios are same, thus law of reciprocal proportion is proved.

### 5.5 Gay-Lussac's law of gaseous volumes [Gay-Lussac-1808] :

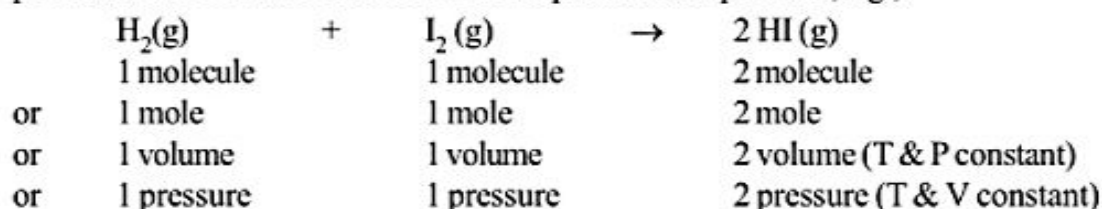
When gases combined or produced in a chemical reaction, they do so in a simple ratio by volume provided all the gases are at same temperature and pressure.

## 6. SIGNIFICANCE OF CHEMICAL EQUATIONS

A chemical equation describes the chemical process both qualitatively and quantitatively. The stoichiometric coefficients in the chemical equation give the quantitative information of the chemical process. These coefficients represent the relative number of molecules or moles of the reactants and products, e.g.,



Again, Avogadro's principle states that under the same conditions of temperature and pressure, equal volumes of gases contain the same number of molecules. Thus, for homogeneous gaseous reactions, the stoichiometric coefficients of the chemical equation also signify the relative volumes of each reactant and product under the same conditions of temperature and pressure, e.g.,





## 6.1 LIMITING REAGENT

The reactant which gives least amount of product on being completely consumed is known as limiting reagent. It may also be defined as the reactant that is completely consumed when a reaction goes to completion. It comes into the picture when reaction involves two or more reactants. For solving such reactions, first step is to calculate Limiting Reagent.

### Calculation of Limiting Reagent:

**Method-I :** By calculating the required amount by the equation and comparing it with given amount.  
[Useful when only two reactant are there]

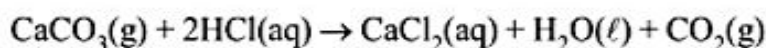
**Method-II :** By calculating amount of any one product obtained taking each reactant one by one irrespective of other reactants. The one giving least product is *limiting reagent*.

**Method-III :** Divide given moles of each reactant by their stoichiometric coefficient, the one with least ratio is *limiting reagent*. [Useful when number of reactants are more than two.]

### Illustration

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If 20gm of  $\text{CaCO}_3$  is treated with 20gm of  $\text{HCl}$ , how many grams of  $\text{CO}_2$  can be generated according to following reaction?



**Sol.** Mole of  $\text{CaCO}_3 = \frac{20}{100} = 0.2$

$$\text{Mole of HCl} = \frac{20}{36.5} = 0.548$$

$$\left[ \frac{\text{Mole}}{\text{Stoichiometric co-efficient}} \right] \text{ for } \text{CaCO}_3 = \frac{0.2}{1} = 0.2$$

$$\left[ \frac{\text{Mole}}{\text{Stoichiometric co-efficient}} \right] \text{ for HCl} = \frac{0.548}{2} = 0.274$$

So  $\text{CaCO}_3$  is limiting reagent

**According to reaction :**

100 gm of  $\text{CaCO}_3$  gives 44gm of  $\text{CO}_2$

$$20 \text{ gm } \text{CaCO}_3 \text{ will give } \frac{44}{100} \times 20 = 8.8 \text{ gm } \text{CO}_2$$

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**Exercise**

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Calculate the mass of carbon tetrachloride can be produced by the reaction of 144gm of carbon with 71 gm of Chlorine.

Ans. 77 gm

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**6.2 PROBLEMS RELATED WITH MIXTURE**

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**Illustration**

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4 gram of a mixture of  $\text{CaCO}_3$  and Sand ( $\text{SiO}_2$ ) is treated with an excess of  $\text{HCl}$  and 0.88 gm of  $\text{CO}_2$  is produced. What is the percentage of  $\text{CaCO}_3$  in the original mixture?

Ans.  $\text{CaCO}_3 + 2\text{HCl} \rightarrow \text{CaCl}_2 + \text{H}_2\text{O} + \text{CO}_2$

$\text{SiO}_2 + \text{HCl} \rightarrow \text{No reaction}$

$\text{CaCO}_3 = x \text{ gm}$

100 gm  $\text{CaCO}_3$  gives  $\longrightarrow$  44 gm  $\text{CO}_2$

$x \text{ gm CaCO}_3$  gives  $\longrightarrow$  0.88 gm  $\text{CO}_2$

$$\Rightarrow \frac{100}{x} = \frac{44}{0.88} \Rightarrow x = 2 \text{ gram}$$

$$\% \text{ CaCO}_3 = \frac{2}{4} \times 100 = 50\%$$


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**Exercise**

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44 gram sample of a natural gas, consisting of methane [ $\text{CH}_4$ ] and ethylene [ $\text{C}_2\text{H}_4$ ] was burned in excess of oxygen yielding 132 gm  $\text{CO}_2$  and some  $\text{H}_2\text{O}$  as products. What is the mole % of ethylene in the sample?

Ans. 50%

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**6.3 PERCENTAGE YIELD**

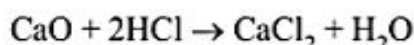
In general, when a reaction is carried out in the laboratory we do not obtain the theoretical amount of product. The amount of product that is actually obtained is called the actual yield. Knowing the actual yield and theoretical yield, the % yield can be calculated by the following formula—

$$\text{Percentage yield} = \frac{\text{Actual yield}}{\text{Theoretical yield}} \times 100\%$$


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**Illustration**

For the reaction



1.12 gram of CaO is reacted with excess of hydrochloric acid and 1.85 gm CaCl<sub>2</sub> is formed. What is the % yield of the reaction?

Sol.  $\text{CaO} + 2\text{HCl} \rightarrow \text{CaCl}_2 + \text{H}_2\text{O}$

56 gm CaO will produce 111 gm CaCl<sub>2</sub>

1.12 gram of CaO will produce  $\rightarrow \frac{111}{56} \times 1.12 = 2.22 \text{ gm}$

Thus Theoretical yield = 2.22 gm

Actual yield = 1.85 gm

$$\% \text{ yield} = \frac{1.85}{2.22} \times 100 = 83.33 \%$$

**Exercise**

Calculate the mass of KCl that is produced from 1 mole of KClO<sub>3</sub> if % yield of reaction is 80?

Ans. 59.6 gm

**6.4 PERCENTAGE PURITY**

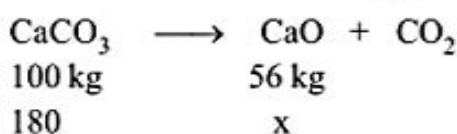
Depending upon the mass of the product, the equivalent amount of reactant present can be determined with the help of given chemical equation. Knowing the actual amount of the reactant taken and the amount calculated with the help of a chemical equation, the purity can be determined, as

$$\text{Percentage purity} = \left[ \frac{\text{Amount of reactant calculated from the chemical equation}}{\text{Actual amount of reactant taken}} \right] \times 100 \%$$

**Illustration**

Calculate the amount of (CaO) in kg that can be produced by heating 200 kg lime stone that is 90% pure CaCO<sub>3</sub>.

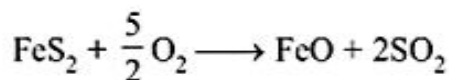
Sol. Mass of Pure CaCO<sub>3</sub> =  $\frac{200 \times 90}{100} = 180 \text{ kg}$



$$\frac{100}{180} = \frac{56}{x} \Rightarrow x = 100.8 \text{ kg}$$

**Exercise**

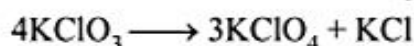
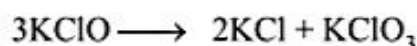
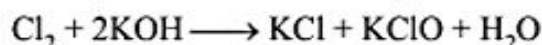
Calculate the mass of coal sample in kg containing 0.05% mass of iron pyrite  $[\text{FeS}_2]$  that can produced 44.8 litre of  $\text{SO}_2$  at 1 atm and 273 with 40% reaction yield?



Ans. 600 kg

**6.5 PROBLEMS RELATED WITH SEQUENTIAL REACTION****Illustration**

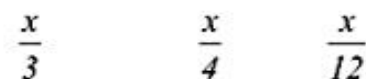
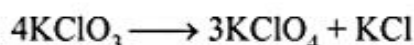
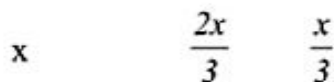
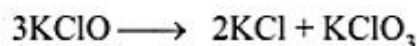
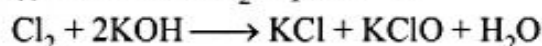
$\text{KClO}_4$  can be prepared by  $\text{Cl}_2$  and  $\text{KOH}$  by a series of reactions as given below



(i) Calculate mass of  $\text{Cl}_2$  in gram required to produce 1385 gm  $\text{KClO}_4$ ?

(ii) Calculate the total mass of  $\text{KCl}$  produced in 1<sup>st</sup>, 2<sup>nd</sup> and 3<sup>rd</sup> reaction?

Sol. (i) Let mole of  $\text{Cl}_2$  required =  $x$



$$\text{Mole of } \text{KClO}_4 \text{ formed} = \frac{1385}{138.5} = 10$$

$$\frac{x}{4} = 10, \qquad x = 40$$

$$\therefore \text{Mass of } \text{Cl}_2 \text{ required for the reaction} = 40 \times 71 = 2840 \text{ gm}$$

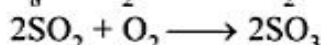
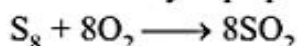
$$(ii) \quad \text{KCl produced from 1<sup>st</sup>, 2<sup>nd</sup> and 3<sup>rd</sup> reaction} = \left( x + \frac{2x}{3} + \frac{x}{12} \right) \text{ mole}$$

$$= \frac{21x}{12} \text{ mole} = \frac{21}{12} \times 40 = 70 \text{ mole}$$

$$\therefore \text{Mass of KCl produced} = 70 \times 74.5 = 5215 \text{ gram}$$

**Exercise**

Sulphur trioxide may be prepared by the following two reactions

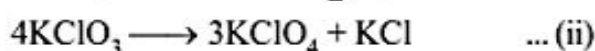
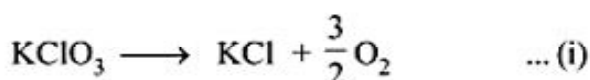


How many gram of  $SO_3$  will be produced from 1 mole of  $S_8$ .

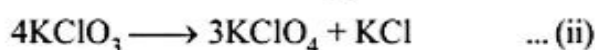
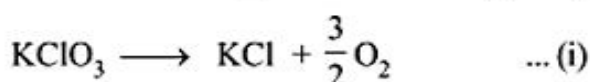
**Ans.** 640 gram

**6.6 PROBLEM RELATED WITH PARALLEL REACTIONS****Illustration**

If 6 moles of  $KClO_3$  are decomposed according to following reactions calculate the moles of  $KClO_4$  produced if mole of  $O_2$  produced are 3?



**Sol.** Let x-mole  $KClO_3$  reacts in reaction (i) and y mole  $KClO_3$  reacts in reaction (ii)



y mole

$$\text{From question} \quad x + y = 6$$

$$\text{and } \frac{3x}{2} = 3$$

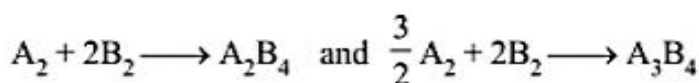
$$\therefore x = 2 \text{ mole} \quad \text{and} \quad y = 4 \text{ mole}$$

It means 4 mole  $KClO_3$  reacts in reaction (ii)

From reaction (ii)

4 mole  $KClO_3$  gives 3 mole  $KClO_4$

**Ans.** 3 mole

**Exercise**

Two substances  $A_2$  and  $B_2$  are allowed to react completely to form  $A_2B_4$  and  $A_3B_4$  mixture, leaving none of the reactions. Using this information. Calculate the composition of final mixture when  $5/4$  mole of  $A_2$  and 2 mole of  $B_2$  is taken?

**Ans.**  $A_3B_4 = 0.5$  mole,  $A_2B_4 = 0.5$  mole

## 6.7 PRINCIPLE OF ATOM CONSERVATION

The principle of conservation of mass, expressed in the concepts of atomic theory means the conservation of atoms. And if atoms are conserved, moles of atoms shall also be conserved. This is known as the principle of atom conservation. This principle is in fact the basis of the mole concept.

In order to solve problems of nearly all stoichiometric calculations, let us first see how this principle works. Choose an example,



Apply the principle of atom conservation (POAC) for K atoms.

Moles of K atoms in reactant = mole of K atoms in products

Moles of K atoms in  $\text{KClO}_3$  = moles of K atoms in  $\text{KCl}$ .

Now, since 1 molecule of  $\text{KClO}_3$  contains 1 atom of K

or 1 mole of  $\text{KClO}_3$  contains 1 mole of K, similarly, 1 mole of  $\text{KCl}$  contains 1 mole of K

Thus, mole of K atoms in  $\text{KClO}_3 = 1 \times \text{moles of } \text{KClO}_3$

and Mole of K atoms in  $\text{KCl} = 1 \times \text{moles of } \text{KCl}$

$\therefore$  mole of  $\text{KClO}_3 = \text{mole of } \text{KCl}$

$$\text{or} \quad \frac{\text{wt. of } \text{KClO}_3 \text{ in g}}{\text{mol. wt. of } \text{KClO}_3} = \frac{\text{wt. of } \text{KCl in g}}{\text{mol. wt. of } \text{KCl}}$$

The above equation gives the weight relationship between  $\text{KClO}_3$  and  $\text{KCl}$  which is important in stoichiometric calculations.

Again, applying the principle of atom conservation for O atoms,

Moles of O in  $\text{KClO}_3 = \text{moles of O in } \text{O}_2$

But since 1 mole of  $\text{KClO}_3$  contains 3 moles of O and 1 mole of  $\text{O}_2$  contains 2 moles of O,

Thus, mole of O in  $\text{KClO}_3 = 3 \times \text{moles of } \text{KClO}_3$

Moles of O in  $\text{O}_2 = 2 \times \text{moles of } \text{O}_2$

$\therefore 3 \times \text{moles of } \text{KClO}_3 = 2 \times \text{moles of } \text{O}_2$

$$\text{or} \quad 3 \times \frac{\text{wt. of } \text{KClO}_3}{\text{mol. wt. of } \text{KClO}_3} = 2 \times \frac{\text{wt. of } \text{O}_2}{\text{mol. wt. of } \text{O}_2}$$

Mole of  $\text{O}_2$  may also be expressed in volume.

### Illustration

All carbon atoms present in  $\text{KH}_3(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$  weighing 254 gm is converted to  $\text{CO}_2$ . How many gram of  $\text{CO}_2$  were obtained?

**Sol.** Apply P.O.A.C. on carbon atom

$4 \times \text{mole of } \text{KH}_3(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O} = 1 \times \text{mole of } \text{CO}_2$

$$4 \times \frac{254}{254} = 1 \times \frac{w_{\text{CO}_2}}{44}$$

$\therefore \text{Mass of } \text{CO}_2 = 4 \times 44 = 176 \text{ gram}$



**Exercise**

A sample of  $\text{KNO}_3$  weighing  $W$ , gram undergo a series of reaction in such a way that all nitrogen atom are converted to  $\text{K}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$ . How many gram of the product were obtained?

[Given M.wt of  $\text{KNO}_3 = M_1$ , M.wt of  $\text{K}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2 = M_2$ ]

Ans.  $\frac{W_1 M_2}{12 M_1}$

**7.1 AVERAGE ATOMIC MASS**

$$\text{Average atomic mass} = \frac{\text{total mass}}{\text{total mole of atoms}}$$

Let a sample contains  $n_1$  mole of atoms with atomic mass  $M_1$  and  $n_2$  mole of atoms with atomic mass  $M_2$ , then

$$M_{av} = \frac{n_1 M_1 + n_2 M_2}{n_1 + n_2}$$

**Illustration**

Find the average atomic mass of a mixture containing 25% by mole  $\text{Cl}^{37}$  and 75% by mole  $\text{Cl}^{35}$ ?

Sol.  $n_1 = 25$        $M_1 = 37$   
 $n_2 = 75$        $M_2 = 35$

$$M_{av} = \frac{25 \times 37 + 75 \times 35}{25 + 75} = 35.5$$

**Exercise**

$\text{Ag}^{107}$  and  $\text{Ag}^{109}$

average atomic mass = 108.5 find % by mole of each isotope

Ans.  $\text{Ag}^{107} = 25\%$ ,  $\text{Ag}^{109} = 75\%$

**7.2 AVERAGE MOLECULAR MASS**

$$\text{Average molecular mass} = \frac{\text{total mass}}{\text{total mole of molecules}}$$

Let a sample contains  $n_1$  mole of molecules with molecular mass  $M_1$  and  $n_2$  mole of molecules with molecular mass  $M_2$ , then

$$M_{av} = \frac{n_1 M_1 + n_2 M_2}{n_1 + n_2}$$

**Illustration**

Air is a mixture of  $O_2$  and  $N_2$  in which  $O_2$  is present 20% by mole and  $N_2$  is present 80% by mole. Find out the average molecular mass of air?

**Sol.**  $n_1 = 20$        $M_1 = 32$   
 $n_2 = 80$        $M_2 = 28$

$$M_{av} = \frac{n_1 M_1 + n_2 M_2}{(n_1 + n_2)} = \frac{20 \times 32 + 80 \times 28}{(20 + 80)} = 28.8$$

**Exercise**

Two gases A and B [M.wt of A = 20 and M. wt of B = 30] are mixed in the mole ratio a : b and the average molecular mass of the gas mixture is 24. What will be the average molar mass of the gas mixture, if gases A and B are mixed in the ratio b : a?

**Ans.** 26

**8. EMPIRICAL & MOLECULAR FORMULA**

Empirical formula of a compound represents the ratio of different atoms present in a molecule.

Molecular formula of a compound represents the exact no. of atoms present in a molecule.

For Hydrogen peroxide, Empirical formula = HO, Molecular formula =  $H_2O_2$

**Steps for writing the empirical formula**

The percentage of the elements in the compound is determined by suitable methods and from the data collected, the empirical formula is determined by the following steps:

- (i) Divide the percentage of each element by its atomic mass. This will give the relative number of moles of atoms of various elements present in the compound.
- (ii) Divide the quotients obtained in the above step by the smallest of them so as to get a simple ratio of moles of various elements.
- (iii) Multiply the figures so obtained, by a suitable integer, if necessary, in order to obtain a whole number ratio.
- (iv) Finally write down the symbols of the various elements side by side and put the above number as the subscripts to the lower right hand corner of each symbol. This will represent the empirical formula of the compound.

**Steps for writing the molecular formula**

- (i) Calculate the empirical formula as described above.
- (ii) Find out the empirical formula mass by adding the atomic masses of all the atoms present in the empirical formula of the compound.
- (iii) Divide the molecular mass (determined experimentally by some suitable method) by the empirical formula mass and find out the value of n.



**Illustration**

Calculate the empirical formula for a compound that contains 26.6% potassium, 35.4% chromium and 38.1% oxygen by mass ?

Given : [Atomic wt : - K = 39; Cr = 52; O = 16]

Sol.	Element	Mass Percentage	Atomic mass	Relative no. of atoms	Simple Ratio
	K	26.6	39	$\frac{26.6}{39} = 0.68$	$\frac{0.68}{0.68} = 1$
	Cr	35.4	52	$\frac{35.4}{52} = 0.68$	$\frac{0.68}{0.68} = 1$
	O	38.1	16	$\frac{38.1}{16} = 2.38$	$\frac{2.38}{0.68} = 3.5$
	K : Cr : O				
	1 : 1 : 3.5				
	2 : 2 : 7 (whole no. ratio)				

Empirical formula :-  $K_2Cr_2O_7$

**Exercise**

A carbon compound containing only carbon and oxygen has an approximate molecular mass of 290. On analysis it is found to contain 50% by mass of each element what is the molecular formula of the compound?

Ans.  $C_{12}O_9$

**9. VAPOUR DENSITY**

Some times in numericals molecular mass of volatile substance is not given, instead vapour density is given. Vapour density can be defined as

$$V.D. = \frac{\text{Density of gas at a given T and P}}{\text{Density of } H_2 \text{ at same T and P}}$$

$$\text{or, } V.D. = \frac{M_{\text{gas}}}{2}$$

$$M_{\text{gas}} = 2 \times V.D.$$

**Illustration**

A compound of nitrogen and oxygen was found to contain 7 : 16 by mass N and O respectively. Calculate molecular formula of the compound if V.D. is 46 ?

**Sol.** Let mass of N = 7 K gram

Mass of O = 16 K gram

Element	Mass	Atomic mass	Relative no. of atoms	Simple ratio
N	7 K	14	$\frac{7K}{14} = 0.5K$	$\frac{0.5K}{0.5K} = 1$
O	16 K	16	$\frac{16K}{16} = K$	$\frac{K}{0.5K} = 2$

N : O = 1 : 2

**Empirical formula = NO<sub>2</sub>**

(Empirical formula)<sub>n</sub> = molecular formula

$$n = \frac{\text{M.mass}}{\text{empirical formula mass}} = \frac{2 \times \text{V.D.}}{46} = \frac{2 \times 46}{46} = 2$$

Molecular formula = (NO<sub>2</sub>)<sub>2</sub> = N<sub>2</sub>O<sub>4</sub>

## 10. EXPERIMENTAL METHODS FOR DETERMINATION OF ATOMIC MASS & MOLECULAR MASS

### 10.1 For determination of atomic mass :-

#### DULONG'S & PETIT'S LAW

In case of heavy solid elements, it is observed that product of atomic mass and specific heat capacity is almost constant.

$$\text{Atomic mass} \times \text{Specific heat capacity (Cal/gm } ^\circ\text{C)} \approx 6.4$$

It should be remembered that this law is an empirical observation and this gives an approximate value of atomic mass.

**Illustration :**

The approximate specific heat capacity of a metal is 0.836 J/gm °C. Find out the approximate atomic mass of the metal?

**Ans.** Atomic mass  $\times$  specific heat  $\approx 6.4$

$$\text{Atomic mass} \approx \frac{6.4}{\text{specific heat}} = \frac{6.4}{0.836/4.2} = 32$$

## 10.2 For determination molecular mass :

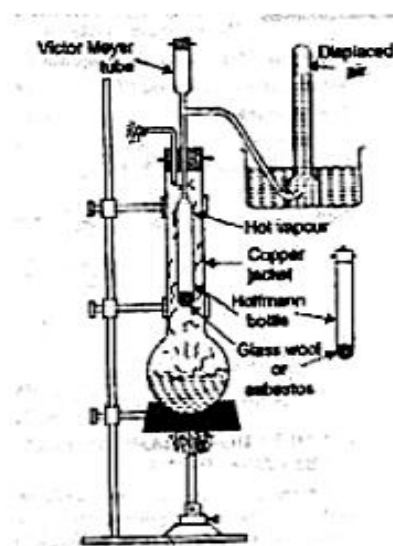
Some of the most commonly used methods for determination of molecular mass are:

- (i) Victor Meyer's Method
- (ii) Silver Salt Method
- (iii) Platinic chloride method

### 10.2.1 VICTOR MEYER'S METHOD

(Applicable for volatile substance)

A known mass of the volatile substance is taken in the Hoffmann's bottle and is vapourised by throwing the Hoffmann's bottle into the Victor Meyer's tube. The vapours displace an equal volume of the moist air and the moist air displaced by the vapours is measured at the room temperature and atmospheric pressure. Following diagram gives the experimental set-up for the Victor - Meyer's process.



Calculations involved

Let the mass of the substance taken be	= W g
Volume of moist vapours collected	= V cm <sup>3</sup>
Room temperature	= T K
Barometric pressure	= P mm
Aqueous tension at T K	= p mm
Pressure of dry vapour	= (P - p) mm.
Calculation of molecular mass(M).	

$$\frac{(P - p)}{760} \times \frac{V}{1000} = \frac{w}{M} \times RT$$

$$M = \frac{w \times RT \times 760 \times 1000}{(P - p) \times V}$$

Applying  $PV = nRT$  for the dry vapour and using  $n = w/M$

#### Vapour pressure of liquid

The pressure exerted by the vapours in equilibrium with its liquid state is called vapour pressure of liquid. In case of liquid water it is also known as aqueous tension.

It depends only on temperature of liquid and is independent of

- (i) Amount of liquid
- (ii) Surface area of liquid
- (iii) Volume of container

**Illustration**

0.15 g of a substance displaced 58.9 cm<sup>3</sup> of air at 300 K and 746 mm pressure. Calculate the molecular mass. (Aq. Tension at 300 K = 26.7 mm).

**Sol.** Mass of the substance = 0.15 g  
 Volume of air displaced (V) = 58.9 cm<sup>3</sup>  
 Temperature (T) = 300 K  
 Pressure (P) = 746 - 26.7 = 719.3 mm

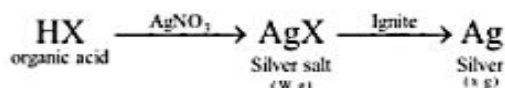
$$\text{Molecular mass} = \frac{719.3}{760} \times \frac{58.9}{1000} = \frac{0.15}{M} \times 0.821 \times 300$$

$$\therefore \text{Molecular mass} = 66.27 \text{ g/mol}$$

**10.2.2 SILVER SALT METHOD**

(Applicable to organic acids only).

A known mass of the acid is dissolved in water followed by the subsequent addition of silver nitrate solution till the precipitation of silver salt is complete. The precipitate is separated, dried, weighed and ignited till decomposition is complete. The residue of pure silver left behind is weighed.

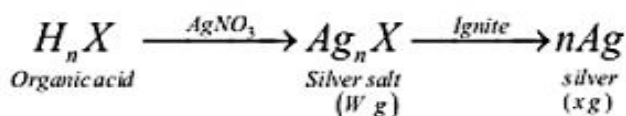


Calculations involved

Let the mass of the silver salt formed = W g

The mass of Ag formed = x g

For polybasic acid of the type H<sub>n</sub>X (n is basicity)



Mass of silver that gives x g of Ag = Wg

Mass of silver that gives n g-atom (108 g) of Ag =  $\frac{108nW}{x}$  g

Molar Mass of salt =  $\frac{108 \times nW}{x}$  g

Molar mass of acid = (molar mass of salt) - n (atomic mass of silver) + n (atomic mass of H)

$$\frac{108 \times nW}{x} - n \times 108 + n \times 1 = n \left( \frac{108W}{x} - 107 \right) \text{ g mol}^{-1}$$

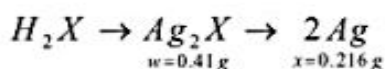


**Illustration**

0.41 g of the silver salt of a dibasic organic acid left a residue to 0.216 g of silver on ignition. Calculate the molecular mass of the acid

**Sol.** Molecular mass of the silver salt taken ( $W$ ) = 0.41 g

Mass of Ag formed ( $x$ ) = 0.216 g



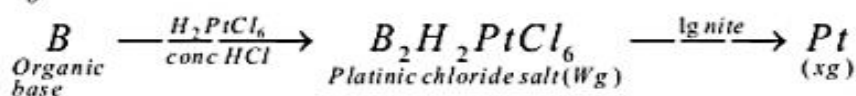
$$\begin{aligned}\text{Now molar mass of acid} &= n \left( \frac{108W}{x} - 107 \right) \text{ g mol}^{-1} \\ &= 2 \left( \frac{108 \times 0.41}{0.216} - 107 \right) \text{ g mol}^{-1} = 196 \text{ g mol}^{-1}\end{aligned}$$

**10.2.3 PLATINIC CHLORIDE METHOD**

(Applicable for finding the molecular masses of organic bases.)

A known mass of organic base is allowed to react with chloroplatinic acid ( $H_2PtCl_6$ ) in presence of conc. HCl to form insoluble platinic chloride. The precipitate of platinic chloride is separated, dried, weighed and is subsequently ignited till decomposition is complete. The residue left is platinum which is again weighed. The molecular mass is then calculated by knowing the mass of the platinic chloride salt and that of platinum left.

If B represents the molecule of monoacidic organic base, then, the formula of platinic chloride salt is  $B_2H_2PtCl_6$

**Calculations involved**

Let the mass of platinic chloride salt =  $W$  g

The mass of platinum residue left =  $x$  g

It may be noted that salt formed with diacidic base would be  $B_2(H_2PtCl_6)_2$ ; with triacidic base would be  $B_2(H_2PtCl_6)_3$  and with polyacidic base would be  $B_2(H_2PtCl_6)_n$

Mass of salt which gives 195 g (1 g-atom) of Pt =  $\frac{W \times 195 \times n}{x}$

Molar mass of salt =  $\frac{W \times 195 \times n}{x} \text{ g mol}^{-1}$

Now from the formula  $B_2(H_2PtCl_6)_n$

$$\text{Molar mass of salt} = [2 \times \text{Molar mass of base}] + n \times [\text{Molar mass of } H_2PtCl_6]$$

$$\begin{aligned}\text{Molar mass of base} &= \frac{1}{2}(\text{Molar mass of salt} - \text{Molar mass of } H_2PtCl_6) \\ &= \frac{1}{2}\left(\frac{W \times 195 \times n}{x} - n \times 410\right) = \frac{n}{2}\left[\frac{W \times 195}{x} - 410\right] \text{ g mol}^{-1}\end{aligned}$$

### Illustration

0.98 g of the chloroplatinate of some diacidic base when ignited left 0.39 g of platinum as residue. What is the molecular mass of the base? (At. Mass of Pt = 195)

**Sol.** Mass of the chloroplatinate salt (W) = 0.98 g

Mass of platinum (x) = 0.39 g

Acidity of the base (n) = 2

$$\text{Now molar mass of the base} = \frac{n}{2}\left(\frac{W \times 195}{x} - 410\right) \text{ g mol}^{-1}$$

$$= \frac{2}{2}\left(\frac{0.98 \times 195}{0.39} - 410\right) \text{ g mol}^{-1} = 80 \text{ g mol}^{-1}$$

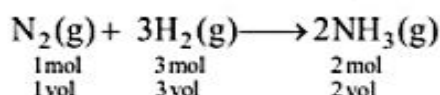
## 11. EUDIOMETRY - GAS ANALYSIS

The study of gaseous reactions is done in a eudiometer tube with the help of Gay-Lussac's law and Avogadro's law. Eudiometer tube is a closed graduated tube open at one end. The other end is a closed one which is provided with platinum terminals for passing electricity for electric spark, through the known volume of mixture of gases and known volume of oxygen gas. Volume of  $CO_2$  formed is determined by absorbing in KOH solution,  $O_2$  is determined by dissolving unreacted  $O_2$  in alkaline pyrogallol and water vapours formed are determined by noting contraction in volume caused due to cooling. Eudiometry helps:

- (i) To study composition of gaseous mixture
- (ii) To study volume – volume relationship
- (iii) To determine molecular formula of gaseous hydrocarbons and
- (iv) To determine molecular formula of gases

### 11.1 GAY LUSSAC LAW

According to Gay - Lussac's law, the volumes of gaseous reactants reacted and the volumes of gaseous products formed, all are measured at the same temperature and pressure, bear a simple ratio.



## 11.2 AVOGADRO'S LAW

In 1812, Amadeo Avogadro stated that samples of different gases which contain the same number of molecules (any complexity, size, shape) occupy the same volume at the same temperature and pressure.

For ideal gas at constant Temperature & Pressure, pressure is directly proportional to no. of moles

## 11.3 SOME ABSORBENTS OF GASES

The absorbent which is used for specific gas is listed below

Absorbent	Gas or gases absorbed
Turpentine oil	O <sub>3</sub>
Alkaline pyrogallol	O <sub>2</sub>
Ferrous sulphate solution	NO
Heated magnesium	N <sub>2</sub>
Heated palladium	H <sub>2</sub>
Ammonical cuprous chloride	O <sub>2</sub> , CO, C <sub>2</sub> H <sub>2</sub> or CH <sub>3</sub> CH
Copper sulphate solution	H <sub>2</sub> S, PH <sub>3</sub> , AsH <sub>3</sub>
Conc. H <sub>2</sub> SO <sub>4</sub>	H <sub>2</sub> O i.e., moisture, NH <sub>3</sub>
NaOH or KOH solution	CO <sub>2</sub> , NO <sub>2</sub> , SO <sub>2</sub> , X <sub>2</sub> , all acidic oxides

## 11.4 VOLUME EXPANSION AND CONTRACTION IN THE EUDIOMETER TUBE



$$\Delta n_g = \text{No. of gaseous products} - \text{No. of gaseous reactants} = (c + d) - (a + b)$$

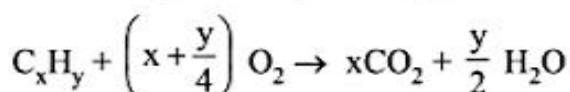
- (a) If  $\Delta n_g > 0$ , then expansion will occur
- (b) If  $\Delta n_g = 0$ , No contraction/expansion (volume remains constant)
- (c) If  $\Delta n_g < 0$ , then contraction will occur

## 11.5 ASSUMPTIONS

- All gases are assumed to be ideal.
- Nitrogen gas formed during reaction will not react with any other gas.
- The volume of solids and liquids are negligible in comparison to the volume of gas.

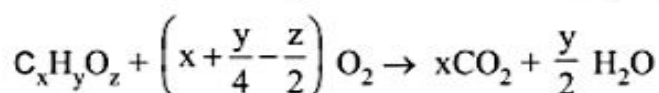
## 11.6 GENERAL REACTIONS FOR COMBUSTION OF ORGANIC COMPOUNDS

- (i) When an organic compound is hydrocarbon :

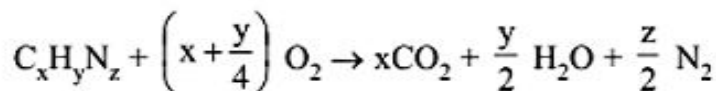




- (ii) When an organic compound contain carbon, hydrogen and oxygen :



- (iii) When an organic compound contain carbon, hydrogen and nitrogen :



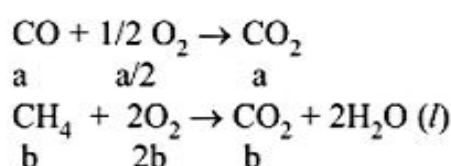
## 11.7 ANALYSIS OF GASEOUS MIXTURE

### Illustration

10 ml of a mixture of CO, CH<sub>4</sub> and N<sub>2</sub>, exploded with excess of oxygen, gave a contraction of 6.5 ml. There was a further contraction of 7 ml when the residual gas was treated with KOH. What is the composition of the original mixture?

**Sol.** Let the volume of CO = a ml  
                                   CH<sub>4</sub> = b ml  
 $\therefore$  N<sub>2</sub> = (10 – a – b) ml

The explosion reactions are



contraction in volume = a + a/2 + b + 2b – a – b = 6.5  
 or, a + 4b = 13 .....(1)

CO<sub>2</sub> is absorbed by KOH solution

$\therefore$  a + b = 7 .....(2)

From equation (1) and (2) a = 5, b = 2

$\therefore$   $\begin{cases} \text{vol. of CO} = 5\text{mL} \\ \text{vol. of CH}_4 = 2\text{mL} \\ \text{vol. of N}_2 = 10 - 5 - 2 = 3\text{mL} \end{cases}$

### Exercise

A mixture of Cl<sub>2</sub> gas (2.8 L) and H<sub>2</sub> gas (3L) was exploded in a eudiometer tube. Calculate the composition by volume of the resulting mixture if all measurements are done under similar conditions of temperature and pressure.

**Ans.** Volume of H<sub>2</sub> gas left behind = 0.2 L, Volume of HCl gas formed = 5.6 L

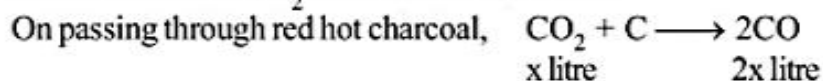


## 11.8 VOLUME - VOLUME ANALYSIS

### Illustration

1 litre of a mixture of CO and CO<sub>2</sub> is taken. This mixture is passed through a tube containing red hot charcoal. The volume now becomes 1.6 litres. The volumes are measured under the same condition. Find the composition of the mixture by volume.

**Sol.** Let the volume of CO<sub>2</sub> in the mixture be x litres



Now, total volume of CO =  $(1 - x) + 2x = 1.6$  (given)

∴  $x = 0.6$  litre

∴ volume of CO<sub>2</sub> in the mixture = 0.6 litre

volume of CO in the mixture =  $1 - 0.6 = 0.4$  litre

### Exercise

60 ml of a mixture of nitrous oxide and nitric oxide was exploded with excess of hydrogen. If 38 ml of N<sub>2</sub> was formed, calculate the volume of each gas in the mixture.

**Ans.** NO = 44 ml

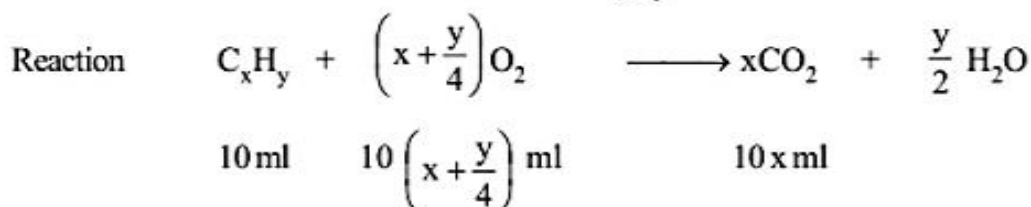
N<sub>2</sub>O = 16 ml **Ans.**

## 11.9 DETERMINATION OF MOLECULAR FORMULA OF GASEOUS HYDROCARBONS

### Illustration

A gaseous hydrocarbon (V.D. = 15) having volume 10 ml was exploded with excess of O<sub>2</sub>. On cooling, a contraction in volume by 25 ml was observed. Calculate the molecular formula of the hydrocarbon.

**Sol.** Let the molecular formula of hydrocarbon = C<sub>x</sub>H<sub>y</sub>



From reaction contraction in volume is given as :  $10 + 10\left(x + \frac{y}{4}\right) - 10x = 25$  (given)

∴  $y = 6$

Now,

Formula of hydrocarbon = C<sub>x</sub>H<sub>6</sub>

Mol. wt. of C<sub>x</sub>H<sub>6</sub> =  $(12 \times x) + (6 \times 1) = 2 \times 15$

∴  $x = 2$

Hence,

Molecular formula of hydrocarbon = C<sub>2</sub>H<sub>6</sub>

**Exercise**

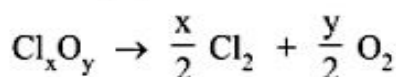
500 ml of a hydrocarbon gas burnt in excess of oxygen yields 2500 ml of  $\text{CO}_2$  and 3.0 litres of water vapours, all the volume being measured at the same temperature and pressure. What is the formula of hydrocarbon gas ?

Ans.  $\text{C}_5\text{H}_{12}$

**11.10 DETERMINATION OF MOLECULAR FORMULA OF GASES****Illustration**

60 ml of a mixture of equal volumes of  $\text{Cl}_2$  and an oxide of chlorine were heated and then cooled back to the original temperature. The resulting gas mixture was found to have a volume of 75 ml. On treatment with caustic soda, the volume contracted to 15 ml. Assuming that all measurements were made at the same temperature & pressure, deduce the simplest formula of the oxide of chlorine. (The oxide of chlorine on heating decomposes quantitatively to give  $\text{O}_2$  &  $\text{Cl}_2$ )

Sol. Let  $\text{Cl}_x\text{O}_y$  be the oxide.



$$1 \text{ Vol.} \quad \frac{x}{2} \text{ Vol.} \quad \frac{y}{2} \text{ Vol.}$$

$$30 \text{ ml} \quad 15x \text{ ml} \quad 15y \text{ ml}$$

Volume of  $\text{Cl}_x\text{O}_y$  = Vol. of  $\text{Cl}_2$  initially = 30 ml

After cooling volume = 75 ml

This corresponds to volume of  $\text{Cl}_2$  initially plus volume of  $\text{Cl}_2$  produced &  $\text{O}_2$  produced.

$$V(\text{Cl}_2) + V(\text{Cl}_2 \text{ produced}) + V(\text{O}_2) = 75 \text{ ml}$$

$\text{NaOH}$  absorbs  $\text{Cl}_2$  apart from  $\text{CO}_2$ . So after  $\text{NaOH}$  treatment, the residual volume corresponds to the volume of  $\text{O}_2 = 15 \text{ ml}$

$$\text{and } V(\text{Cl}_2 \text{ produced}) = 75 - V(\text{Cl}_2) - V(\text{O}_2) = 75 - 30 - 15 = 30 \text{ ml}$$

$$15x = 30 \Rightarrow x = 2$$

$$\text{and } 15y = 15 \Rightarrow y = 1$$

Hence, formula of oxide of chloride is  $\text{Cl}_2\text{O}$ .

**Exercise**

50 ml of pure and dry oxygen was subjected to silent electric discharge and on cooling to the original temperature, the volume of ozonised oxygen was found to be 47 ml. The gas was then brought in contact with turpentine oil, the remaining gas occupied a volume of 41 ml. Find the molecular formula of ozone.

Ans.  $\text{O}_3$

## 12. CONCENTRATION TERMS

A solution is a homogeneous mixture of two or more substances, the composition of which may vary within limits. "A solution is a special kind of mixture in which substances are intermixed so intimately that they can not be observed as separate components". The substance which is to be dissolved is called **solute** while the medium in which the solute is dissolved to get a homogeneous mixture is called the **solvent**. A solution is termed as binary and ternary if it consists of two and three components respectively.

### 12.1 METHODS OF EXPRESSING CONCENTRATION OF SOLUTION

Concentration of solution is the amount of solute dissolved in a known amount of the solvent or solution. The concentration of solution can be expressed in various ways as discussed below.

**12.1.1 Percentage :** It refers to the amount of the solute per 100 parts of the solution. It can also be called as parts per hundred (pph). It can be expressed by any of following four methods :

$$(i) \text{ Weight by weight percentage (\% w/w)} = \frac{\text{Wt. of solute (g)}}{\text{Wt. of solution (g)}} \times 100$$

e.g., 10%  $\text{Na}_2\text{CO}_3$  solution w/w means 10g of  $\text{Na}_2\text{CO}_3$  is dissolved in 100g of the solution. (It means 10g  $\text{Na}_2\text{CO}_3$  is dissolved in 90 of solvent)

$$(ii) \text{ Weight by volume percent (\% w/v)} = \frac{\text{Wt. of solute (g)}}{\text{Volume of solution (cm}^3\text{)}} \times 100$$

e.g., 10%  $\text{Na}_2\text{CO}_3$  (w/v) means 10g  $\text{Na}_2\text{CO}_3$  is dissolved in 100  $\text{cm}^3$  of solution.

$$(iii) \text{ Volume by volume percent (\% v/v)} = \frac{\text{Volume of solute (cm}^3\text{)}}{\text{Volume of solution (cm}^3\text{)}} \times 100$$

e.g., 10% ethanol (v/v) means 10 $\text{cm}^3$  of ethanol dissolved in 100  $\text{cm}^3$  of solution.

$$(iv) \text{ Volume by weight percent (\% v/w)} = \frac{\text{Vol. of solute}}{\text{Wt. of solution}} \times 100$$

e.g., 10% ethanol (v/w) means 10 $\text{cm}^3$  of ethanol dissolved in 100g of solution.



**Illustration**

Concentrated nitric acid used as laboratory reagent is usually 69% by mass of nitric acid. Calculate the volume of the solution which contains 23 g nitric acid. The density of concentrated acid is  $1.41 \text{ g cm}^{-3}$ .

**Sol.** Given  $\text{HNO}_3$  is 69% by mass;

density of  $\text{HNO}_3 = 1.41 \text{ g cm}^{-3}$ .

Thus (i) 69 g  $\text{HNO}_3$  is present in conc.  $\text{HNO}_3 = 100 \text{ g}$

23 g  $\text{HNO}_3$  is present in conc.  $\text{HNO}_3 = \frac{100}{69} \times 23 = 33.33 \text{ g}$

(ii) Volume of solution required =  $\frac{\text{Mass}}{\text{Density}} = \frac{33.33}{1.41} = 23.64 \text{ mL}$

**Exercise**

Calculate % w/w of NaOH in a solution containing 40% w/v NaOH. Density of solution is  $d \text{ (g/ml)}$ .

**Ans.** % by mass =  $\frac{40}{d} \%$

**12.1.2 Parts per million (ppm) and parts per billion (ppb) :** When a solute is present in very small quantity, it is convenient to express the concentration in parts per million and parts per billion. It is the number of parts of solute per million ( $10^6$ ) or per billion ( $10^9$ ) parts of solution. It is independent of the temperature.

$$\text{ppm} = \frac{\text{Mass of solute component}}{\text{Total mass of solution}} \times 10^6$$

$$\text{ppb} = \frac{\text{Mass of solute component}}{\text{Total mass of solution}} \times 10^9$$

**Illustration**

Calculate the parts per million of  $\text{SO}_2$  gas in 250 ml water (density  $1 \text{ g cm}^{-3}$ ) containing  $5 \times 10^{-4} \text{ g}$  of  $\text{SO}_2$  gas.

**Sol.** Mass of  $\text{SO}_2$  gas =  $5 \times 10^{-4} \text{ g}$ ;

Mass of  $\text{H}_2\text{O}$  = Volume  $\times$  Density =  $250 \text{ cm}^3 \times 1 \text{ g cm}^{-3} = 250 \text{ g}$

$\therefore$  Parts per million of  $\text{SO}_2$  gas =  $\frac{5 \times 10^{-4}}{250 \text{ g}} \times 10^6 = 2$

**Exercise**

Units of parts per million (ppm) or per billion (ppb) are often used to describe the concentrations of solutes in very dilute solutions. The units are defined as the number of grams of solute per million or per billion grams of solvent. Bay of Bengal has 1.9 ppm of lithium ions. What is the molality of  $\text{Li}^+$  in this water?

**Ans.**  $2.7 \times 10^{-4}$

**12.1.3 Normality (N) :** It is defined as the number of gram equivalents of a solute present per litre of the solution. Unit of normality is gram equivalents  $\text{litre}^{-1}$ . Normality changes with temperature since it involves volume. When a solution is diluted  $x$  times, its normality also decreases by  $x$  times. Concentration in terms of normality is generally expressed as,

$N$  = Normal solution;  $5N$  = Penta normal,  $10N$  = Deca normal;

$N/2$  = semi normal;  $N/10$  = Deci normal;  $N/5$  = Penti normal

$N/100$  or  $0.01 N$  = centinormal,  $N/1000$  or  $0.001$  = millinormal.

Mathematically normality can be calculated by following formulas,

(i) Normality

$$N = \frac{\text{Number of gram equivalents of solute}}{\text{Volume of solution}(\ell)} = \frac{\text{Weight of solute in gram}}{\text{equivalent weight of solute} \times \text{Volume of solution}(\ell)}$$

$$= \frac{\text{wt. of solute}}{\text{eq. wt. of solute}} \times \frac{1000}{\text{wt. of solution (ml)}}$$

$$\text{Equivalent weight of solute} = \frac{\text{Gram molar mass}}{\text{Acidity/Basicity/Cation valency}}$$

Acidity = No. of replaceable  $\text{OH}^-$  in a molecule of a base

For example : Acidity of  $\text{NaOH} = 1$

Basicity = No. of replaceable  $\text{H}^+$  in a molecule of an acid

For example : Basicity of  $\text{H}_2\text{SO}_4 = 2$

(ii) If volume  $V_1$  and normality  $N_1$  is so changed that new normality is  $N_2$  and volume is  $V_2$  then,

$$\boxed{N_1 V_1 = N_2 V_2} \quad (\text{No. of equivalents remains same in mixing and dilution})$$

(iii) When two solutions of the same solute and solvent are mixed then normality of mixture ( $N$ ) is

$$\boxed{N = \frac{N_1 V_1 + N_2 V_2}{V_1 + V_2}}$$

**Illustration**

Calculate normality of 7g/L  $\text{H}_2\text{SO}_4$ .

**Sol.**  $N_{\text{H}_2\text{SO}_4} = \frac{\text{g/L}}{\text{Eq.wt.}} = \frac{7}{49} = \frac{1}{7} = 0.143 \text{ g eq l}^{-1}$

**Exercise**

How many grams of oxalic acid are to be dissolved in 250 ml water to prepare 0.1 N solution?  
(Eq. wt. of ox. acid = 63)

**Ans.** 1.575g

**12.1.4 Molarity (M) :** Molarity of a solution is the number of moles of the solute per litre of solution (or number of millimoles per ml of solution). Unit of molarity is mol/litre or  $\text{mol/dm}^3$ . For example, a molar (1M) solution of sugar means a solution containing 1 mole of sugar per litre of the solution. Solutions in terms of molarity is generally expressed as,

1M = One molar solution, 2M = Molarity is two,  $\frac{M}{2}$  or 0.5M = Semimolar solution,

$\frac{M}{10}$  or 0.1M = Decimolar solution,  $\frac{M}{100}$  or 0.01 M = Centimolar solution

$\frac{M}{1000}$  or 0.001 M = Millimolar solution

Mathematically, molarity can be calculated by following formulas :

(i)  $M = \frac{\text{No. of moles of solute}(n)}{\text{Vol. of solution in litres}} = \frac{\text{wt. of solute (gm)}}{\text{gm mol.wt. of solute}} \times \frac{1000}{\text{wt. of solution (ml)}}$

(ii) If molarity and volume of the solution are changed from  $M_1, V_1$  to  $M_2, V_2$ . Then,

$$M_1 V_1 = M_2 V_2$$

(iii) In balanced chemical equation, if  $n_1$  moles of reactant-1 react with  $n_2$  moles of reactant-2 . Then,



$$\frac{M_1 V_1}{n_1} = \frac{M_2 V_2}{n_2}$$

(iv) If two solutions of the same solute are mixed then molarity (M) of resulting solution

$$M = \frac{M_1 V_1 + M_2 V_2}{(V_1 + V_2)}$$

**Illustration**

A bottle of commercial sulphuric acid (density  $1.787 \text{ g ml}^{-1}$ ) is labelled as 86% by weight. What is the molarity of acid?

**Sol.** (i) Molarity of  $\text{H}_2\text{SO}_4 = \frac{\text{Wt. of } \text{H}_2\text{SO}_4 \text{ in 1L solution}}{\text{mol. wt. of } \text{H}_2\text{SO}_4}$

But wt. of given  $\text{H}_2\text{SO}_4$  per litre  $= \frac{86}{100} \times 1.787 \times 1000 = 1536.82 \text{ g}$ .

Hence molarity of  $\text{H}_2\text{SO}_4 = \frac{1536.82}{98} = 15.68 \text{ mol L}^{-1}$

**Exercise**

A sample contains  $\text{I}_2$  and benzene. The mole fraction of  $\text{I}_2 = 0.2$ . Calculate molarity of solution if

(i) density of solution is  $d \text{ gm/ml}$       (ii) density of  $\text{I}_2$  & benzene are  $d_{\text{I}_2}$  &  $d_{\text{benzene}}$

**Ans.** (i)  $M = 1.77 d$       (ii)  $M = \frac{0.2}{\left( \frac{50.8}{d_{\text{I}_2}} + \frac{62.4}{d_{\text{benzene}}} \right)} \times 1000$

**12.1.5 Formality (F) :** Formality of solution may be defined as the number of gram formula units of the ionic solute dissolved per litre of the solution. It is represented by **F**. Commonly, the term formality is used to express the concentration of the ionic solids which do not exist as molecules but exist as network of ions. A solution containing one gram formula mass of solute per litre of the solution has formality equal to one and is called **Formal solution**. It may be mentioned here that the formality of a solution changes with change in temperature.

$$\begin{aligned} \text{Formality (F)} &= \frac{\text{Number of gram formula units of solute}}{\text{Volume of solution in litres}} \\ &= \frac{\text{Mass of ionic solute (g)}}{\text{gram formula unit mass of solute} \times \text{Volume of solution (l)}} \end{aligned}$$

**Illustration**

What will be the formality of  $\text{KNO}_3$  solution having strength equal to  $2.02 \text{ g per litre}$  ?

**Sol.** Strength of  $\text{KNO}_3 = 2.02 \text{ gL}^{-1}$   
and g formula weight of  $\text{KNO}_3 = 101 \text{ g}$

$$\therefore \text{Formality of } \text{KNO}_3 = \frac{\text{strength in gL}^{-1}}{\text{g. formula wt. of } \text{KNO}_3} = \frac{2.02}{101} = 0.02 \text{ F}$$



### Exercise

Calculate the formality of NaCl solution, 5.85 g of which have been dissolved to form 250 ml of the given solution

Ans. 0.4 F

**12.1.6 Molality (m) :** It is the number of moles of the solute per 1000g of the solvent. Unit of molality is mol/kg. For example, a 0.2 molal (0.2m) solution of glucose means a solution obtained by dissolving 0.2 mole of glucose in 1000 gm of water. Molality (m) does not depend on temperature since it involves measurement of weight of liquids.

Mathematically molality can be calculated by following formulas,

$$(i) \ m = \frac{\text{Number of moles of solute}}{\text{Weight of solvent in kg}} = \frac{\text{Number of moles of solute}}{\text{Weight of solvent in gm}} \times 1000$$

$$(ii) = \frac{\text{Wt. of solute}}{\text{Mol. wt. of solute}} \times \frac{1000}{\text{Weight of solvent in gm}}$$

### Illustration

The density of a 3 M  $\text{Na}_2\text{S}_2\text{O}_3$  solution is  $1.25 \text{ g ml}^{-1}$ . Calculate percentage by mass of  $\text{Na}_2\text{S}_2\text{O}_3$  and molalities of  $\text{Na}^+$  and  $\text{S}_2\text{O}_3^{2-}$  ions.

**Sol.** (i) Total mass of  $\text{Na}_2\text{S}_2\text{O}_3$  solution = Vol of solution  $\times$  Density of solution  
 $= 1000 \text{ ml} \times 1.25 \text{ g ml}^{-1} = 1250 \text{ g}$

Wt. of 3M  $\text{Na}_2\text{S}_2\text{O}_3$  in 1000 ml solution =  $3 \times \text{Mol. wt of } \text{Na}_2\text{S}_2\text{O}_3 (158) = 474 \text{ g}$   
 $[\because \text{Mol. wt. of } \text{Na}_2\text{S}_2\text{O}_3 = 158 \text{ g mol}^{-1}]$

$$\therefore \% \text{ of } \text{Na}_2\text{S}_2\text{O}_3 = \frac{\text{Wt. of } \text{Na}_2\text{S}_2\text{O}_3}{\text{Total wt. of solution}} \times 100 = \frac{474}{1250} \times 100 = 37.92\%$$

(ii) To find molality of  $\text{Na}^+$  ions  
 $\because 3 \text{ M } \text{Na}_2\text{S}_2\text{O}_3$  contain 6 moles of  $\text{Na}^+$  ions in one litre

$$\therefore \text{Molality of } \text{Na}^+ \text{ ions} = 6 \times \frac{1000}{\text{wt. of solvent } (1250 - 474 = 776 \text{ g})} = 6 \times \frac{1000}{776} = 7.73 \text{ m}$$

(iii) To find molality of  $\text{S}_2\text{O}_3^{2-}$   
 $\because 3 \text{ M } \text{Na}_2\text{S}_2\text{O}_3$  contain 3 moles of  $\text{S}_2\text{O}_3^{2-}$  ions in one litre

$$\text{Molality of } \text{S}_2\text{O}_3^{2-} = 3 \times \frac{1000}{\text{wt. of solvent} = 776} = 3.865 \text{ m}$$



**Exercise**

Find molality of 40% by mass (w/w) NaOH.

Ans.  $\frac{50}{3} \text{ m}$

**12.1.7 Mole fraction ( $\chi$ ) :** Mole fraction may be defined as the ratio of number of moles of one component to the total number of moles of all the components (solvent and solute) present in the solution. It is denoted by the letter  $\chi$ . It may be noted that the mole fraction is independent of the temperature. Mole fraction is dimensionless. If a solution contains the components A and B and suppose that  $W_A$  gram of A and  $W_B$  gram of B are present in it.

Number of moles of A is given by,  $n_A = \frac{W_A}{M_A}$  and the number of moles of B is given by,  $n_B = \frac{W_B}{M_B}$

where  $M_A$  and  $M_B$  are molecular mass of A and B respectively.

Total number of moles of A and B =  $n_A + n_B$

Mole fraction of A,  $\chi_A = \frac{n_A}{n_A + n_B}$

Mole fraction of B,  $\chi_B = \frac{n_B}{n_A + n_B}$

The sum of mole fractions of all the components in the solution is always one.

$$\chi_A + \chi_B = \frac{n_A}{n_A + n_B} + \frac{n_B}{n_A + n_B} = 1$$

$$\chi_A + \chi_B = 1$$

Thus, if we know the mole fraction of one component of a binary solution, the mole fraction of the other can be calculated.

**Illustration**

Find out the masses of acid and water required to prepare 1 mole of  $\text{CH}_3\text{COOH}$  solution of 0.3 mole fraction of  $\text{CH}_3\text{COOH}$ .

Sol.  $\chi_{\text{CH}_3\text{COOH}} = 0.3$

$$\chi_{\text{H}_2\text{O}} = 1 - 0.3 = 0.7$$

$$\text{Wt. of } \text{CH}_3\text{COOH} = \chi_{\text{CH}_3\text{COOH}} \times \text{mol. wt.}(\text{CH}_3\text{COOH}) = 0.3 \times 60 = 18 \text{ g}$$

$$\text{Wt. of water} = \chi_{\text{H}_2\text{O}} \times \text{mol. wt.}(\text{H}_2\text{O}) = 0.7 \times 18 = 12.6 \text{ g}$$

**Exercise**

Mole fraction of a solute in benzene is 0.2. Find out the molality of the solution.

**Ans.**  $3.2 \text{ mol kg}^{-1}$

**12.1.8 Mass Fraction :** Mass fraction of a component in a solution is the mass of the component divided by the total mass of the solution. For a solution containing  $w_A$  gm of A and  $w_B$  gm of B.

$$\text{Mass fraction of A} = \frac{w_A}{w_A + w_B}$$

$$\text{Mass fraction of B} = \frac{w_B}{w_A + w_B}$$

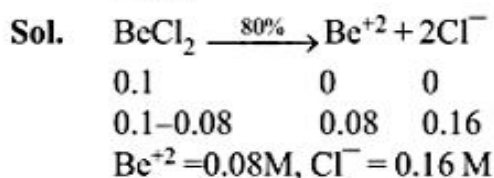
**Note :** It may be noted that molality, mole fraction, mass fraction etc. are preferred to molarity, normality, formality etc. Because the former involve the weights of the solute and solvent where as later involve volumes of solutions. Temperature has no effect on weights but it has significant effect on volumes.

## 12.2 MOLARITY OF IONIC COMPOUNDS

In ionic compounds, calculate the dissociated mole of each ion per mole of molecule considering the degree of dissociation.

**Illustration**

Find the molarity of various ions in 0.1 M  $\text{BeCl}_2$  solution, considering degree of dissociation of  $\text{BeCl}_2$  as 80%.

**Exercise**

Calculate 'm' of all the ions present in the solution of  $\text{Al}_2(\text{SO}_4)_3$  for 1M solution.

Given  $d_{\text{solution}} = 2.342 \text{ gm/ml}$ .

**Ans.**  $\text{Al}^{3+} = 1\text{m}, \text{SO}_4^{2-} = 1.5\text{m}$

## 12.3 MIXING OR DILUTION OF SOLUTIONS

### Illustration

20 ml N/2 HCl, 60 ml N/10 H<sub>2</sub>SO<sub>4</sub> and 150 ml N/5 HNO<sub>3</sub> are mixed together. Calculate the normality of the [H<sup>+</sup>] in final solution.

**Sol.**  $N_1V_1 + N_2V_2 + N_3V_3 = NV$

$$\left(\frac{1}{2} \times 20\right) + \left(\frac{1}{10} \times 60\right) + \left(\frac{1}{5} \times 150\right) = N(230)$$

$$10 + 6 + 30 = N(230)$$

$$46 = N(230)$$

$$N = 0.2$$

### Exercise

200 ml of 1M HCl solution is mixed with 800 ml of 2M HCl solution.

(a) Calculate the final molarity of the solution.

(b) If density of final solution is 1.2 gm/ml. Calculate molality 'm'

**Ans** (a) 1.8M, (b) 1.5 m

## 12.4 MIXING OF ACID & BASE SOLUTIONS

In case of mixing of acid and base, calculate equivalent or milliequivalent of acid and base separately, subtract the lower value from higher value, which gives the number of equivalent in the final solution.

### Illustration

50 ml N/2 HCl, 50 ml N/5 H<sub>2</sub>SO<sub>4</sub> and 200 ml N/10 NaOH are mixed. What will be normality of [H<sup>+</sup>] ions?

**Sol.** meq of acids =  $\left(50 \times \frac{1}{2}\right) + \left(50 \times \frac{1}{5}\right) = 25 + 10 = 35$

$$\text{meq of base} = 200 \times \frac{1}{10} = 20$$

$$\text{After mixing meq of acid} = 35 - 20 = 15$$

$$\therefore \text{Normality of H}^+ \text{ ion, } N = \frac{15}{300} = 0.05 \text{ Ans.}$$

### Exercise

Calculate [H<sup>+</sup>] in a solution if 0.2 M 100 ml H<sub>2</sub>SO<sub>4</sub> is mixed with 0.1 M 300 ml NaOH solution.

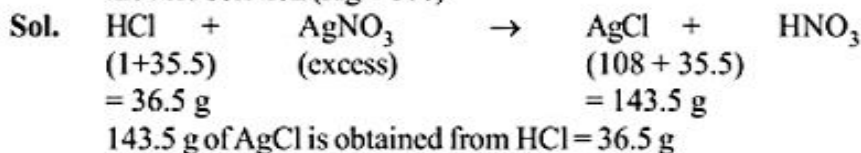
**Ans.** 0.025M

## 12.5 PROBLEM INVOLVING PRECIPITATION

In problems involving precipitation, complete reaction is assumed and the limiting reagent completely reacts. Ions in the precipitated product is not considered in finding concentration of that ions.

**Illustration**

10 ml of HCl solution gave 0.1435 g of AgCl when treated with excess of AgNO<sub>3</sub>. Find the molarity of the acid solution (Ag = 108)



$$0.1435 \text{ g of AgCl is obtained from HCl} = \frac{36.5}{143.5} \times 0.1435 \text{ g} = 0.0365$$

$$\therefore \text{Molarity of HCl solution} = \frac{0.0365}{36.5} \times \frac{1000}{10} = 0.1 \text{ M}$$

**Exercise**

If 200 ml of 0.1 NaCl is mixed with 100 ml of 0.2 M AgNO<sub>3</sub> solution. Calculate molarity of all the ions in the final solution.

**Ans.**  $\text{Na}^+ = 0.067 \text{ M}, \text{NO}_3^- = 0.067 \text{ M}$

**12.6 SOME TYPICAL CONCENTRATION TERMS****12.6.1 Strength of H<sub>2</sub>O<sub>2</sub> solution :**

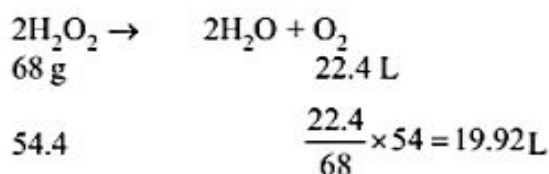
The strength of H<sub>2</sub>O<sub>2</sub> is aqueous solution is expressed in the following two ways :

- Percentage strength :** The mass of H<sub>2</sub>O<sub>2</sub> present in 100 ml of the aqueous solution is termed as percentage strength. For example, a 25% solution (w/v) of H<sub>2</sub>O<sub>2</sub> means that 25 grams of H<sub>2</sub>O<sub>2</sub> are present in 100 ml of the solution.
- Volume strength :** Strength of the sample of H<sub>2</sub>O<sub>2</sub> is generally expressed in terms of the volume of oxygen at 0°C and 1 atm that one volume of the sample of hydrogen peroxide gives on heating. The commercial samples are marked as '10 volume', '15 volume' or '20 volume'. 10 volume means that one volume of the sample of hydrogen peroxide gives 10 volumes of oxygen at 0°C and 1 atm. 1 ml of a 10 volume solution of H<sub>2</sub>O<sub>2</sub> will liberate 10 ml of oxygen at 0°C and 1 atm.

**Illustration**

Find the volume strength of 1.6 M H<sub>2</sub>O<sub>2</sub> solution.

**Sol.** Strength of the solution = Molarity  $\times$  mol. mass =  $1.6 \times 34 = 54.4 \text{ gL}^{-1}$



$$\therefore \text{Volume strength} = '19.92 \text{ V}'$$



**Exercise**

For '44.8 V'  $\text{H}_2\text{O}_2$  solution having  $d = 1.136 \text{ g/ml}$  calculate

(i) Molarity of  $\text{H}_2\text{O}_2$  solution.

(ii) Mole fraction of  $\text{H}_2\text{O}_2$  solution.

**Ans.** (i) 4 M ; (ii) 0.06

**12.6.2 Percentage labelling of oleum**

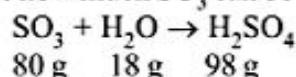
Oleum is fuming sulphuric acid which contains extra  $\text{SO}_3$  dissolved in  $\text{H}_2\text{SO}_4$ . To convert this extra  $\text{SO}_3$  into  $\text{H}_2\text{SO}_4$ , water has to be added ( $\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$ ). The amount of sulphuric acid obtained when just sufficient water is added into 100 g of oleum so that all  $\text{SO}_3$  present in it is converted into  $\text{H}_2\text{SO}_4$  is called percentage labelling of oleum.

**Illustration**

**Sol.** An oleum is labelled as 109%. Calculate mass percent of free  $\text{SO}_3$  and  $\text{H}_2\text{SO}_4$

It means that water added = 9 g in 100 gm oleum

Let us calculate how much  $\text{SO}_3$  can be converted into  $\text{H}_2\text{SO}_4$  by 9 g of water



i.e., 9 g  $\text{H}_2\text{O}$  can dissolve 40 g  $\text{SO}_3$  to form 49 g  $\text{H}_2\text{SO}_4$

$\therefore$  Mass of  $\text{SO}_3$  in 100 g oleum = 40 g

and % by mass of  $\text{SO}_3 = 40 \%$

and % by mass of  $\text{H}_2\text{SO}_4 = 60 \%$

**Exercise**

A mixture is prepared by mixing 10 gm  $\text{H}_2\text{SO}_4$  and 40 gm  $\text{SO}_3$  calculate,

(a) mole fraction of  $\text{H}_2\text{SO}_4$

(b) % labelling of oleum

**Ans.** (a) 0.169; (b) 118 %

**12.7 RELATIONSHIP BETWEEN DIFFERENT CONCENTRATION TERMS**

$$1. \quad N = M \times n \text{ factor}$$

$$2. \quad M = \frac{md}{1 + mM_2/1000}$$

$$3. \quad m = \frac{1000 \times x_2}{x_1 M_1}$$

$$4. \quad M = \frac{1000dx_2}{x_1 M_1 + x_2 M_2}$$

$$5. \quad d = M \left( \frac{1}{m} + \frac{M_2}{1000} \right)$$

$$6. \quad \text{Volume strength of } \text{H}_2\text{O}_2 = 5.6 \times N = \frac{5.6 \times \text{Percentage strength}}{\text{Eq.wt. of } \text{H}_2\text{O}_2 (17)} \times 10$$

7. Volume strength of  $\text{H}_2\text{O}_2 = 11.2 \times M = \frac{11.2 \times \text{Percentage strength} \times 10}{\text{Mol.wt. of } \text{H}_2\text{O}_2 (34)}$

8. In oleum labelled as  $(100 + x) \%$

$$\% \text{ of free } \text{SO}_3 = \left( \frac{80 \times x}{18} \right) (\text{w/w})$$

where N = Normality

M = Molarity

d = density of solution

$x_2$  = Mole fraction of solute

$M_1$  = Molecular mass of solvent

m = molality

$M_2$  = Molecular mass of solute

$x_1$  = Mole fraction of solvent

d = Density of solution.

## SOLVED EXAMPLES

**Q.1** Naturally occurring chlorine is 75.53%  $\text{Cl}^{35}$  which has an atomic mass of 34.969 amu and 24.47%  $\text{Cl}^{37}$  which has a mass of 36.966 amu. Calculate the average atomic mass of chlorine-

- (A) 35.5 amu                      (B) 36.5 amu                      (C) 71 amu                      (D) 72 amu

**Ans.** (A)

**Sol.** Average atomic mass =  $\frac{\% \text{ of I isotope} \times \text{its atomic mass} + \% \text{ of II isotope} \times \text{its atomic mass}}{100}$

$$= \frac{75.53 \times 34.969 + 24.47 \times 36.96}{100}$$

$$= 35.5 \text{ amu.}$$

**Q.2** How many carbon atoms are present in 0.35 mol of  $\text{C}_6\text{H}_{12}\text{O}_6$  -

- (A)  $6.023 \times 10^{23}$  carbon atoms                      (B)  $1.26 \times 10^{23}$  carbon atoms  
(C)  $1.26 \times 10^{24}$  carbon atoms                      (D)  $6.023 \times 10^{24}$  carbon atoms

**Ans.** (C)

**Sol.**  $\therefore$  1 mol of  $\text{C}_6\text{H}_{12}\text{O}_6$  has =  $6 N_A$  atoms of C  
 $\therefore$  0.35 mol of  $\text{C}_6\text{H}_{12}\text{O}_6$  has  
 =  $6 \times 0.35 N_A$  atoms of C  
 =  $2.1 N_A$  atoms  
 =  $2.1 \times 6.022 \times 10^{23} = 1.26 \times 10^{24}$  carbon atoms

**Q.3** Calculate the mass in gm of  $2N_A$  molecules of  $\text{CO}_2$  -

- (A) 22 gm                      (B) 44 gm                      (C) 88 gm                      (D) None of these.

**Ans.** (C)

**Sol.**  $\therefore N_A$  molecules of  $\text{CO}_2$  has molecular mass = 44 gm  
 $\therefore 2N_A$  molecules of  $\text{CO}_2$  has molecular mass =  $44 \times 2 = 88$  gm.

**Q.4** How many years it would take to spend Avogadro's number of rupees at the rate of 1 million rupees in one second -

- (A)  $19.098 \times 10^{19}$  years                      (B) 19.098 years  
(C)  $19.098 \times 10^9$  years                      (D) None of these

**Ans.** (C)

**Sol.**  $\therefore 10^6$  rupees are spent in 1 sec.

$$\therefore 6.022 \times 10^{23} \text{ rupees are spent in } = \frac{1 \times 6.022 \times 10^{23}}{10^6} \text{ sec}$$

$$= \frac{1 \times 6.022 \times 10^{23}}{10^6 \times 60 \times 60 \times 24 \times 365} \text{ years} = 19.098 \times 10^9 \text{ year}$$

**Q.5** Calculate the number of  $\text{Cl}^-$  and  $\text{Ca}^{+2}$  ions in 222 g anhydrous  $\text{CaCl}_2$ .

- (A)  $2N_A$  ions of  $\text{Ca}^{+2}$  &  $4N$  ions of  $\text{Cl}^-$                       (B)  $2N_A$  ions of  $\text{Cl}^-$  &  $4N$  ions of  $\text{Ca}^{+2}$   
(C)  $1N_A$  ions of  $\text{Ca}^{+2}$  &  $1N$  ions of  $\text{Cl}^-$                       (D) None of these.

**Ans.** (A)

**Sol.**  $\therefore$  mol. wt. of  $\text{CaCl}_2 = 111$  g  
 $\therefore 111$  g  $\text{CaCl}_2$  has =  $N_A$  ions of  $\text{Ca}^{+2}$   
 $\therefore 222$ g of  $\text{CaCl}_2$  has  $\frac{N_A \times 222}{111} = 2N_A$  ions of  $\text{Ca}^{+2}$

Also  $\therefore$  111 g  $\text{CaCl}_2$  has  $= 2N_A$  ions of  $\text{Cl}^-$

$\therefore$  222 g  $\text{CaCl}_2$  has  $= \frac{2N_A \times 222}{111}$  ions of  $\text{Cl}^- = 4N_A$  ions of  $\text{Cl}^-$ .

**Q.6** What is the molecular mass of a substance, each molecule of which contains 9 carbon atoms, 13 hydrogen atoms and  $2.33 \times 10^{-23}$  g of other component?

**Ans.** 135.04

**Sol.** The molecule has C, H and other component.

Mass of 9 C atoms  $= 12 \times 9 = 108$  amu

Mass of 13 H atoms  $= 13 \times 1 = 13$  amu

Mass of other component  $= \frac{2.33 \times 10^{-23}}{1.66 \times 10^{-24}} = 14.04 \text{ amu}$

$\therefore$  Total mass of one molecule  $= 108 + 13 + 14.04 = 135.04$  amu

$\therefore$  Mol. mass of substance  $= 135.04$

**Q.7** The density of  $\text{O}_2$  at  $0^\circ\text{C}$  and 1 atm is 1.429 g / litre. The molar volume of gas is -  
(A) 22.4 lit. (B) 11.2 lit (C) 33.6 lit (D) 5.6 lit.

**Ans.** (A)

**Sol.**  $\therefore$  1.429 gm of  $\text{O}_2$  gas occupies volume = 1 litre.

$\therefore$  32 gm of  $\text{O}_2$  gas occupies  $= \frac{32}{1.429} = 22.4$  litre/mol.

**Q.8** How many molecules are in 5.23 gm of glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) -  
(A)  $1.65 \times 10^{22}$  (B)  $1.75 \times 10^{22}$  (C)  $1.75 \times 10^{21}$  (D) None of these

**Ans.** (B)

**Sol.**  $\therefore$  180 gm glucose has  $= N_A$  molecules

$\therefore$  5.23 gm glucose has  $= \frac{5.23 \times 6.022 \times 10^{23}}{180} = 1.75 \times 10^{22}$  molecules

**Q.9** How many g of S are required to produce 10 moles and 10g of  $\text{H}_2\text{SO}_4$  respectively?

**Ans.** 320 g, 3.265 g

**Sol.**  $\therefore$  1 mole of  $\text{H}_2\text{SO}_4$  has  $= 32$  g S

$\therefore$  10 mole of  $\text{H}_2\text{SO}_4$  has  $= 32 \times 10 = 320$  g S

Also, 98g of  $\text{H}_2\text{SO}_4$  has  $= 32$  g S

$\therefore$  10 g of  $\text{H}_2\text{SO}_4$  has  $= (32 \times 10)/98 = 3.265$  g S

**Q.10** P and Q are two elements which form  $\text{P}_2\text{Q}_3$  and  $\text{PQ}_2$  molecules. If 0.15 mole of  $\text{P}_2\text{Q}_3$  and  $\text{PQ}_2$  weighs 15.9 g and 9.3g, respectively, what are atomic mass of P and Q?

**Ans.** P = 26, Q = 18

**Sol.** Let at. mass of P and Q be a and b respectively,

$\therefore$  Mol. mass of  $\text{P}_2\text{Q}_3 = 2a + 3b$

and Mol. mass of  $\text{PQ}_2 = a + 2b$

$\therefore (2a + 3b) \times 0.15 = 15.9$

and  $(a + 2b) \times 0.15 = 9.3$

$a = 26, b = 18$

atomic mass of P = 26

atomic mass of Q = 18



**Q.11** A hydrate of iron (III) thiocyanate  $\text{Fe}(\text{SCN})_3$ , was found to contain 19%  $\text{H}_2\text{O}$ . What is the formula of the hydrate?

**Ans.**  $\text{Fe}(\text{SCN})_3 \cdot 3\text{H}_2\text{O}$

**Sol.** Let the hydrate be  $\text{Fe}(\text{SCN})_3 \cdot m\text{H}_2\text{O}$

Molecular mass of hydrate =  $56 + 3 \times (32 + 12 + 14) + 18m = 230 + 18m$

$$\therefore \% \text{ of } \text{H}_2\text{O} = \frac{18m \times 100}{230 + 18m} = 19 \quad \text{or} \quad m = 2.99 \approx 3$$

$\therefore$  Formula is  $\text{Fe}(\text{SCN})_3 \cdot 3\text{H}_2\text{O}$

**Q.12** The vapour density of a mixture containing  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  is 38.3 at  $27^\circ\text{C}$ . Calculate the mole of  $\text{NO}_2$  in 100 mole mixture.

**Ans.** 33.48

**Sol.** Mol. mass of mixture of  $\text{NO}_2$  and  $\text{N}_2\text{O}_4 = 38.3 \times 2 = 76.6$

Let a mole of  $\text{NO}_2$  be present in 100 mole mixture

= mass of  $\text{NO}_2$  + mass of  $\text{N}_2\text{O}_4$  = mass of mixture,

$$a \times 46 + (100 - a) \times 92 = 100 \times 76.6$$

$$\therefore a = 33.48 \text{ mole}$$

**Q.13** What is the weight of  $3.01 \times 10^{23}$  molecules of ammonia -

(A) 17 gm (B) 8.5 gm (C) 34 gm (D) None of these

**Ans.** (B)

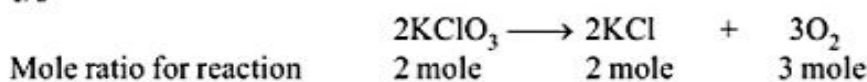
**Sol.**  $\therefore 6.022 \times 10^{23}$  molecules of  $\text{NH}_3$  has weight = 17 gm

$$\therefore 3.01 \times 10^{23} \text{ molecules of } \text{NH}_3 \text{ has weight} = \frac{17 \times 3.01 \times 10^{23}}{6.022 \times 10^{23}} = 8.50 \text{ gm}$$

**Q.14** How many moles of potassium chlorate to be heated to produce 5.6 litre oxygen at  $0^\circ\text{C}$  and 1 atm ?

**Ans.** 1/6

**Sol.**



$\therefore 3 \times 22.4$  litre  $\text{O}_2$  is formed by 2 mole  $\text{KClO}_3$

$$5.6 \text{ litre } \text{O}_2 \text{ is formed by } \frac{2 \times 5.6}{3 \times 22.4} = 1/6 \text{ mole } \text{KClO}_3$$

**Q.15** How many molecules are present in 1 ml of water vapours at  $0^\circ\text{C}$  and 1 atm -

(A)  $1.69 \times 10^{19}$  (B)  $2.69 \times 10^{-19}$  (C)  $1.69 \times 10^{-19}$  (D)  $2.69 \times 10^{19}$

**Ans.** (D)

**Sol.**  $\therefore 22.4$  litre water vapour at  $0^\circ\text{C}$  and 1 atm has =  $6.022 \times 10^{23}$  molecules

$$\therefore 1 \times 10^{-3} \text{ litre water vapours has} = \frac{6.022 \times 10^{23}}{22.4} \times 10^{-3} = 2.69 \times 10^{19}$$

**Q.16** Calculate the weight of lime ( $\text{CaO}$ ) obtained by heating 200 kg of 95% pure lime stone ( $\text{CaCO}_3$ ).

(A) 104.4 kg (B) 105.4 kg

(C) 212.8 kg (D) 106.4 kg

**Ans.** (D)

**Sol.** 100 kg impure sample has pure  $\text{CaCO}_3 = 95 \text{ kg}$

$$\therefore 200 \text{ kg impure sample has pure } \text{CaCO}_3 = \frac{95 \times 200}{100} = 190 \text{ kg.}$$



$\therefore 100 \text{ kg } \text{CaCO}_3 \text{ gives } \text{CaO} = 56 \text{ kg.}$

$$\therefore 190 \text{ kg } \text{CaCO}_3 \text{ gives } \text{CaO} = \frac{56 \times 190}{100} = 106.4 \text{ kg.}$$

**Q.17** Zinc and hydrochloric acid react according to the reaction :



If 0.30 mole of Zn are added to hydrochloric acid containing 0.52 mole HCl, how many moles of  $\text{H}_2$  are produced?

**Ans.** 0.26



Initial moles    0.30    0.52                      0            0

Final moles    0.04    0                      0.26    0.26

Moles of  $\text{H}_2$  produced = 0.26

**Q.18** 4 g of an impure sample of  $\text{CaCO}_3$  on treatment with excess HCl produces 0.88 g  $\text{CO}_2$ . What is percent purity of  $\text{CaCO}_3$  sample?

**Ans.** 50%



44g  $\text{CO}_2 \equiv 100 \text{ g } \text{CaCO}_3$

$$0.88 \text{ g } \text{CO}_2 \equiv \frac{100 \times 0.88}{44} = 2.0 \text{ g } \text{CaCO}_3$$

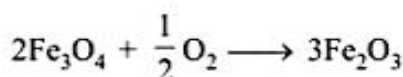
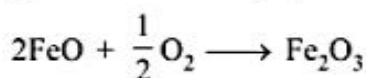
$$\therefore \text{Percentage purity} = \frac{2}{4} \times 100 = 50\%$$

**Q.19** A mixture of FeO and  $\text{Fe}_3\text{O}_4$  when heated in air to constant weight gains 5% in its weight. Find out composition of mixture.

**Ans.** FeO = 20.28%,

$\text{Fe}_3\text{O}_4 = 79.72\%$

**Sol.** Let weight of FeO and  $\text{Fe}_3\text{O}_4$  be a and b g, respectively.



$\therefore 144 \text{ g FeO gives } 160 \text{ g } \text{Fe}_2\text{O}_3$

$\therefore a \text{ g FeO gives } 160 \times a/144 \text{ g } \text{Fe}_2\text{O}_3$

Similarly, weight of  $\text{Fe}_2\text{O}_3$  formed by  $\text{Fe}_3\text{O}_4 = \frac{160 \times 3b}{464}$

$$\text{Now if } a + b = 100 ; \text{ then } \frac{160 \times a}{144} + \frac{160 \times 3b}{464} = 105$$

Solving these two equations :  $a = 21.06$  and  $b = 78.94$

Percentage of FeO  $\approx 20.28\%$  and percentage of  $\text{Fe}_3\text{O}_4 \approx 79.72\%$

- Q.20** The reaction,  $2C + O_2 \longrightarrow 2CO$  is carried out by taking 24 g of carbon and 96g  $O_2$ , find out:  
 (A) Which reactant is left in excess?  
 (B) How much of it is left  
 (C) How many mole of CO are formed?  
 (D) How many g of carbon should be taken so that nothing is left at the end of the reaction?



$$\text{Mole before reaction} \quad \frac{24}{12} = 2 \quad \frac{96}{32} = 3 \quad 0$$

$$\text{Mole after reaction} \quad 0 \quad 2 \quad 2$$

(A)  $\therefore O_2$  is left in excess.

(B) 2 mole of  $O_2$  or 64 g  $O_2$  is left.

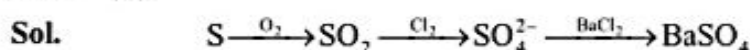
(C) 2 mole of CO or 56 g CO is formed.

(D) To use  $O_2$  completely total 6 mole of carbon or 72 g carbon is needed.

- Q.21** 8g of sulphur are burnt to form  $SO_2$ , which is oxidised by  $Cl_2$  water. The solution is treated with  $BaCl_2$  solution. The amount of  $BaSO_4$  precipitated is :

(A) 1.0 mole (B) 0.5 mole (C) 0.75 mole (D) 0.25 mole

**Ans.** (D)



$$\text{Mole of } BaSO_4 \text{ formed} = \text{moles of sulphur} = \frac{8}{32} = \frac{1}{4}$$

- Q.22** 8 litre of  $H_2$  and 6 litre of  $Cl_2$  are allowed to react to maximum possible extent. Find out the final volume of reaction mixture. Suppose P and T remains constant throughout the course of reaction-  
 (A) 7 litre (B) 14 litre (C) 2 litre (D) None of these.

**Ans.** (B)



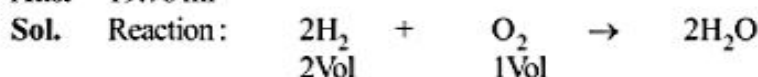
$$\text{Volume before reaction} \quad 8 \text{ lit} \quad 6 \text{ lit} \quad 0$$

$$\text{Volume after reaction} \quad 2 \quad 0 \quad 12$$

$$\therefore \text{Volume after reaction} = \text{Volume of } H_2 \text{ left} + \text{Volume of HCl formed} \\ = 2 + 12 = 14 \text{ lit}$$

- Q.23** When measured at the same temperature and pressure, hydrogen reacts with oxygen to form water in the volume ratio 2 : 1. Calculate the volume of  $O_2$  gas measured at  $137^\circ C$  and 760 mm pressure that will combine with 100 ml of  $H_2$  at  $0^\circ C$  and 200 mm pressure.

**Ans.** 19.76 ml



$$2 \text{ volume of } H_2 \text{ required } O_2 = 1 \text{ Vol}$$

$$\therefore 100 \text{ mL of } H_2 \text{ required } O_2 = \frac{100}{2} = 50 \text{ ml at } 0^\circ C \text{ and } 200 \text{ mm}$$

$$\therefore P_1 = 200 \text{ mm}, V_1 = 50 \text{ mL}, T_1 = 0 + 273 = 273 \text{ K}, P_2 = 760 \text{ mm}, V_2 = ?, T_2 = 137 + 273 = 410 \text{ K}$$

But,

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \text{ (gas equation)}$$



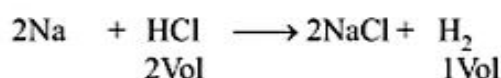
Hence, 
$$V_2 = \frac{P_1 V_1 T_2}{P_2 T_1}$$

$$\therefore V_2 = \frac{200\text{mm} \times 50\text{mL} \times 410\text{K}}{760\text{mm} \times 273\text{K}} = 19.76 \text{ ml Ans.}$$

**Q.24** A gaseous mixture containing 49.5 ml of hydrogen chloride and  $\text{H}_2$  gases was kept in contact with Na/Hg. The volume of mixture decreased to 42 ml. If 99.5 ml of the same mixture is mixed 49.5 ml of gaseous ammonia and then exposed to water, calculate the final volume. All measurements of volume being done under same conditions of temperature and pressure.

**Ans.** 60.5 ml

**Sol.** Volume of  $\text{H}_2$  gas +  $\text{HCl}$  (g) = 49.5 mL. When kept in contact with Na/Hg only HCl will react with Na as follows :



Reduction in volume = 2 Vol – 1 Vol = 1 Vol for 2 Vol of HCl

Actual reduction in volume = 49.5 – 42 = 7.5 ml

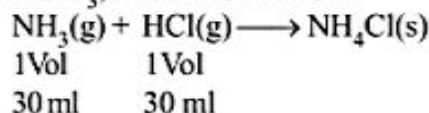
$\therefore$  Volume of HCl present in 49.5 ml mixture = 7.5  $\times$  2 = 15 ml

Volume of  $\text{H}_2$  = 49.5 – 15 = 34.5 ml

$\therefore$  99.5 mL of mixture would contain  $\text{HCl}$ (g) = 15  $\times$   $\frac{99.5}{49.5}$  = 30 ml

and  $\text{H}_2$  = 99.5 – 30 = 69.5 ml

When mixed with  $\text{NH}_3$ , the reaction will be :



$\therefore$  Residual  $\text{NH}_3$  = 49.5 – 30 = 19.5 ml

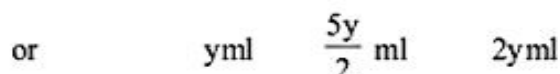
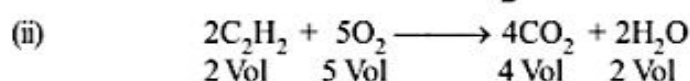
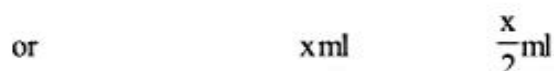
It will also dissolve in  $\text{H}_2\text{O}$ . So, only gas left behind is  $\text{H}_2$  gas. Hence :

Residual  $\text{H}_2$  = 99.5 – 30 = 69.5 mL or final volume = **69.5 ml**

**Q.25** A mixture of ethyne ( $\text{C}_2\text{H}_2$ ) and  $\text{H}_2$  was mixed with 65 ml of  $\text{O}_2$  and exploded in a eudiometer tube. On cooling, it was found to have undergone a contraction of 35 ml. When treated with a KOH solution, a further contraction of 34 ml took place and 15 ml of  $\text{O}_2$  alone was left behind. Find the percentage composition of ethyne and  $\text{H}_2$  in the mixture.

**Ans.**  $\text{C}_2\text{H}_2$  = 53.2 %,  $\text{H}_2$  = 46.8%

**Sol.** Let mixture contains  $\text{H}_2$  = x ml and  $\text{C}_2\text{H}_2$  = y ml



From question

$$2y = 34 \Rightarrow y = 17$$

and,  $\frac{x}{2} + \frac{5y}{2} = 65 - 17$

$$\therefore x = 15$$

$$\therefore x = 2 \times 7.5 = 15.0 \text{ ml}$$

Thus, volume of  $\text{H}_2 = 15.0 \text{ mL}$ ; volume of  $\text{C}_2\text{H}_2 = 17 \text{ ml}$

$$\therefore \% \text{ age of } \text{H}_2 = \frac{\text{Vol. of } \text{H}_2}{\text{Vol. of } \text{H}_2 + \text{Vol. of } \text{C}_2\text{H}_2} \times 100$$

$$= \frac{15}{15+17} \times 100 = 46.8$$

$$\therefore \% \text{ age of } \text{C}_2\text{H}_2 = 100 - 46.88 = 53.2$$

**Q.26** 0.9 g of a solid organic compound (molecular weight 90) containing carbon, hydrocarbon and oxygen, was heated with oxygen corresponding to a volume of 224 ml at S.T.P. After combustion, the total volume of the gases was 560 ml at S.T.P. On treatment with potassium hydroxide, the volume decreased to 112 ml. Determine the molecular formula of the compound.

**Ans.**  $\text{C}_2\text{H}_2\text{O}_4$

**Sol.** Let the formula of organic compound containing C, H and oxygen =  $\text{C}_x\text{H}_y\text{O}_z$

On combustion,  $\text{CO}_2$  and  $\text{H}_2\text{O}$  (zero volume at  $0^\circ\text{C}$ ) are formed

So, the residual gas will contain  $\text{CO}_2$  and unused  $\text{O}_2$ .

Since  $\text{CO}_2$  gas is absorbed by  $\text{KOH}$ , the volume of  $\text{CO}_2$  formed =  $560 - 112 = 448 \text{ ml}$

Volume of  $\text{O}_2$  used =  $224 - 112 = 112 \text{ ml}$

$$\text{Mole of } \text{CO}_2 = \frac{1}{22400} \times 448$$

$$\text{No. of mole of compound} = \frac{0.9}{90} = 0.01 \text{ mol}$$

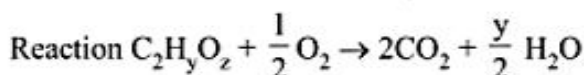
$$\therefore 0.01 \text{ mole compound produced} = 0.02 \text{ mole of } \text{CO}_2$$

$$1 \text{ mole compound produced } \text{CO}_2 = 0.2 \times \frac{1}{0.01} = 2 \text{ mol } \text{CO}_2$$

$$\therefore 2 \text{ mol } \text{CO}_2 \equiv 2 \text{ mol C atoms}$$

$$\therefore \text{Formula of compound} = \text{C}_2\text{H}_y\text{O}_z$$

$$\text{Mol. wt. of } \text{C}_2\text{H}_y\text{O}_z = (2 \times 12) + 1 \times y + 16 \times z = 24 + y + 16z$$



Atoms of oxygen involved in the above reaction are :

$$z + 1 = 4 + \frac{y}{2}; z = 4 + \frac{y}{2} - 1 = 3 + \frac{y}{2}$$

$$\therefore z = 3 + \frac{y}{2}$$

But mol. wt.  $24 + y + 16z = 90$



Hence  $24 + y + 16 \left( 3 + \frac{y}{2} \right) = 90$   
 $y = 2$

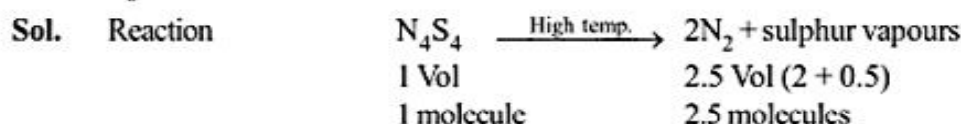
Substituting the value of  $y = 2$

$$z = 3 + \frac{2}{2} = 4$$

$\therefore$  Molecular formula of compound =  $C_2H_yO_z = C_2H_2O_4$  Ans.

- Q.27** At high temperatures, the compound  $S_4N_4$  decomposes completely into  $N_2$  and sulphur vapours. If all measurements are made under the same conditions of temperature and pressure, it is found that for each volume of  $S_4N_4$  decomposed 2.5 volumes of gaseous products are formed. What is the molecular formula of sulphur?

**Ans.**  $S_8$



2.5 molecules of  $N_2$  + sulphur vapours = 4 atoms of nitrogen + 0.5 molecule of sulphur vapour. Hence the formula  $S_4N_4$  indicates that :

0.5 molecule of sulphur contains S-atoms = 4

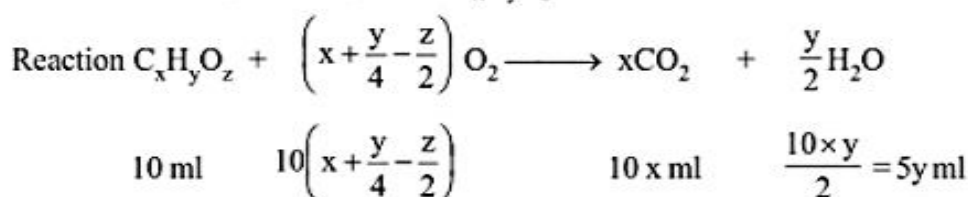
$$1 \text{ molecule of sulphur contains S-atoms} = \frac{4}{0.5} = 8$$

$\therefore$  Formula of sulphur =  $S_8$

- Q.28** 10 ml of a gaseous organic compound containing C, H and O only was mixed with 100 ml of oxygen and exploded under conditions which allowed the water formed to condense. The volume of the gas after explosion was 90 ml. On treatment with potash solution, a further contraction in volume of 20 ml was observed. Given that the vapour density of the compound is 23, deduce the molecular formula. All volume measurements were carried out under the same conditions.

**Ans.**  $C_2H_6O$

**Sol.** Let formula of organic compound =  $C_xH_yO_z$



(a) Since potash solution (KOH) absorbs  $CO_2$ , so volume of  $CO_2$  gas = 20 ml.  
 $10x = 20$ ;  $x = 2$

(b) Contraction in volume after explosion and cooling as obtained from reaction

$$10 + 10 \left( x + \frac{y}{4} - \frac{z}{2} \right) - 10x = 10 + 100 - 90 = 20 \text{ ml (given)}$$

$$10 + 10 \left( 2 + \frac{y}{4} - \frac{z}{2} \right) - (10 \times 2) = 20$$

$$5y - 10z = 20$$

.....(1)

But mol. wt. of  $C_xH_yO_z$  or  $C_2H_yO_z = (2 \times 12) + (y \times 1) + (16 \times z)$   
 $= 24 + y + 16z = 2 \times 23$  (given)  
 or  $y + 16z = 46 - 24 = 22$  .....(2)

From (1) and (2)  $z = 1$   
 $y = 6$

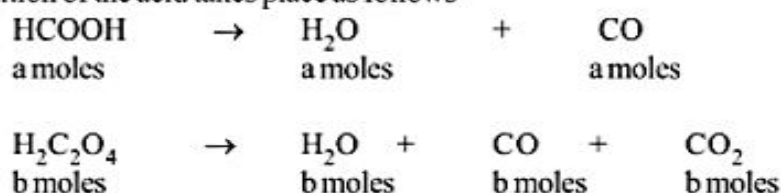
Since  $x = 2$ ,  $y = 6$  and  $z = 1$ , the molecular formula of  $C_xH_yO_z = C_2H_6O$

- Q.29** A mixture of formic acid and oxalic acid is heated with concentrated  $H_2SO_4$ . The gas produced is collected and on its treatment with KOH solution the volume of the gas decreased by one-sixth. Calculate the molar ratio of the two acids in the original mixture.

**Ans.** 4 : 1

**Sol.** Let moles of  $HCOOH$  and  $H_2C_2O_4$  are  $a$  and  $b$  respectively

The decomposition of the acid takes place as follows



$H_2O$  is absorbed by  $H_2SO_4$  and  $CO_2$  is absorbed by KOH.

Thus as given,  $\frac{\text{volume of } CO_2}{\text{total volume of } (CO + CO_2)} = \frac{b}{a + b + b} = \frac{1}{6}$

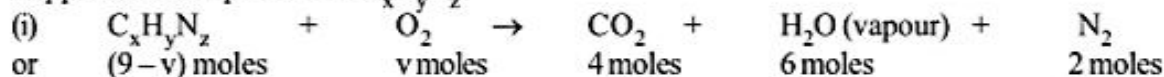
or  $\frac{a}{b} = 4$

Molar ratio of  $HCOOH$  and  $H_2C_2O_4 = 4 : 1$

- Q.30** 9 volumes of a gaseous organic compound A and just sufficient amount of oxygen required for its complete combustion, yielded, 4 volume of  $CO_2$ , 6 volumes of water vapour and 2 volumes of  $N_2$ , all volumes measured at the same temperature and pressure. If the compound A contained only C, H and N, (i) how many volumes of oxygen are required for complete combustion, and (ii) what is the molecular formula of the compound A?

**Ans.** (i) 7 volume (ii)  $C_2H_6N_2$

**Sol.** Suppose the compound A is  $C_xH_yN_z$

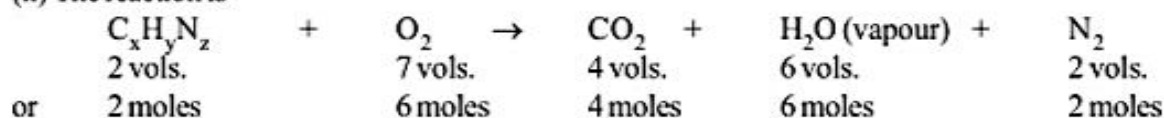


Applying POAC for O atoms,

$$2 \times \text{moles of } O_2 = 2 \times \text{moles of } CO_2 + 1 \times \text{moles of } H_2O$$

$$2v = 2 \times 4 + 1 \times 6 = 14; v = 7 \text{ volumes}$$

(ii) The reaction is



Applying POAC for C, H and N, we get respectively

$$x \times \text{moles of } C_xH_yN_z = 1 \times \text{moles of } CO_2$$

$$x \times 2 = 1 \times 4; x = 2$$

$$y \times \text{moles of } C_xH_yN_z = 2 \times \text{moles of } H_2O \text{ (vapour)}$$

$$y \times 2 = 2 \times 6; y = 6$$

$$z \times \text{moles of } C_xH_yN_z = 2 \times \text{moles of } N_2$$

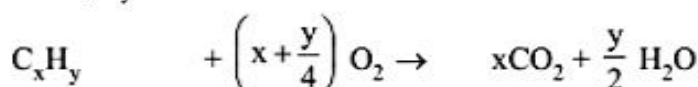
$$z \times 2 = 2 \times 2; z = 2$$

Hence the compound is  $C_2H_6N_2$

- Q.31** 15 ml of gaseous hydrocarbon required for complete combustion 357 ml of air (21% of  $O_2$  by volume) and the gaseous products occupied 327 ml (all volumes being measured at S.T.P.). What is the formula of hydrocarbon?

**Ans.**  $C_3H_8$

**Sol.** Let  $C_xH_y$  be the hydrocarbon



$$1 \text{ Vol.} \quad \left(x + \frac{y}{4}\right) \text{ Vol.} \quad x \text{ Vol.}$$

From equation, the contraction

$$= 1 + (x + y/4) - (x + 0) = 1 + y/4$$

for 15 ml gas, contraction =

$$15(1 + y/4) = (15 + 357) - (327) = 45$$

$$y = 8$$

The gaseous products after contraction = 327

This includes vol. of  $CO_2$  plus volume of  $N_2$  in the air ( $O_2$  is completely used up). So calculate the volume of  $N_2$  in the air.

$$\text{Vol. of } O_2 = 0.21 \times 357 = 75 \text{ ml}$$

$$\text{Vol. of } N_2 = 357 - 75 = 282 \text{ ml}$$

$$\text{Now, Vol. of } N_2 + \text{Vol. of } CO_2 = 327 \text{ ml}$$

$$\text{Vol. of } CO_2 = 327 - 282 = 45 \text{ ml}$$

$$\text{The volume of } CO_2 \text{ produced} = 15x$$

$$15x = 45$$

$$x = 3$$

Hence the hydrocarbon is  $C_3H_8$

- Q.32** Calculate the molarity and molality of a solution of  $H_2SO_4$  (sp. gr. = 1.98) containing 27%  $H_2SO_4$  by mass.

**Ans.** 3.3 M, 3.77 M

$$\text{Sol. Vol of 100 g of 27\% } H_2SO_4 = \frac{\text{wt.}}{d} = \frac{100}{1.98} \text{ ml}$$

$$M_{H_2SO_4} = \frac{\text{wt. / mol.wt.}}{\text{vol. of solution (litre)}} = \frac{27 \times 1.98 \times 1000}{98 \times 100} = 3.3 \text{ mol } L^{-1}$$

$$m_{H_2SO_4} = \frac{\text{wt. / mol.wt.}}{\text{wt. of solvent (kg)}} = \frac{27 \times 1000}{(100 - 27) \times 98} = 3.77 \text{ mol } Kg^{-1}$$

**Q.33** How many milliliter of concentrated sulphuric acid of density  $1.84 \text{ g ml}^{-1}$  containing 98%  $\text{H}_2\text{SO}_4$  by mass are required to make (a) 4 litre of 1 N solution and (b) 200 mL of 0.25 M solution.

**Ans.** (a) 108.7 (b) 2.72 ml

**Sol.** (a) Gram eq. wt. of  $\text{H}_2\text{SO}_4 = \frac{98}{2} = 49 \text{ g.}$

To find wt. of  $\text{H}_2\text{SO}_4$  (W) required to prepare 4 L of 1N  $\text{H}_2\text{SO}_4$ , we have :

$$1 = \frac{\text{wt. of } \text{H}_2\text{SO}_4}{\text{g. eq. wt. of } \text{H}_2\text{SO}_4 \times 4(l)} = \frac{\text{wt. of } \text{H}_2\text{SO}_4}{49 \times 4(l)}$$

Or wt. of  $\text{H}_2\text{SO}_4 = 196 \text{ g.}$

Since acid is 98% thus amount of solution =  $\frac{196 \times 100}{98} = 200 \text{ g.}$

Thus, volume (mass/density) of 98%  $\text{H}_2\text{SO}_4$  solution =  $\frac{200}{1.84} = 108.7 \text{ ml}$

$$(b) 0.25 = \frac{\text{wt. of } \text{H}_2\text{SO}_4 \times 1000}{\text{g. mol. wt. of } \text{H}_2\text{SO}_4 \times \text{vol. of solution in ml}}$$

$$\therefore \text{wt. of } \text{H}_2\text{SO}_4 = \frac{0.25 \times 98 \times 200}{1000} = 4.9 \text{ g}$$

$$\therefore \text{wt. of 98\% } \text{H}_2\text{SO}_4 \text{ solution} = \frac{4.9 \times 100}{98} = 5 \text{ g}$$

$$\text{Volume of } \text{H}_2\text{SO}_4 \text{ solution} = \frac{\text{Mass}}{\text{Density}} = \frac{5}{1.84} = 2.72 \text{ ml}$$

**Q.34** Derive the relation between molality (m) and mole fraction of solute,  $\chi_2$

**Sol.** Molality, m means, m mole of solute in 1000 g of solvent which is equal to  $1000/M_1$  mol where  $M_1$  = molar mass of the solvent.

$$\therefore \text{Mole fraction, } \chi_2 = \frac{\text{moles of solute}}{\text{Moles of solute} + \text{Moles of solvent}} = \frac{m}{m + \frac{1000}{M_1}} = \frac{mM_1}{mM_1 + 1000}$$

$$\text{Hence } m = \frac{1000 \times \chi_2}{(1 - \chi_2)}$$

**Q.35** The molality and molarity of a solution of  $\text{H}_2\text{SO}_4$  are 94.13 and 11.12 respectively. Calculate the density of the solution.

**Ans.** 1.2079 g/ml

$$\text{Sol. } d = M \left( \frac{1}{m} + \frac{\text{mol.wt.}}{1000} \right) = 11.12 \left( \frac{1}{94.13} + \frac{98}{1000} \right) = 1.2079 \text{ g/ml}$$



**Q.36** Calculate the (a) molarity (b) normality of the phosphoric acid solution (sp. gravity 1.426 and containing 60% by weight of pure  $\text{H}_3\text{PO}_4$ . Atomic mass of P = 31)

**Ans.** (a) 8.73 M (b) 26.19 N

**Sol.** Weight of  $\text{H}_3\text{PO}_4$  in 100 g solution = 60 g; Weight of water =  $100 - 60 = 40$  g

(a) Calculation of molarity

Molecular mass of  $\text{H}_3\text{PO}_4 = 98 \text{ g mol}^{-1}$

$$\text{Molarity} = \frac{60}{98} \times \frac{1.426 \times 1000}{100} = 8.73 \text{ M}$$

(b) Normality = Molarity  $\times$  Basicity =  $8.73 \times 3 = 26.19 \text{ N}$

**Q.37** Upon heating a litre of  $\frac{\text{M}}{2}$  HCl solution, 2.675 g hydrogen chloride is lost due to evaporation and the volume of the solution shrinks to 750 ml. Calculate

(i) the molarity of the resulting solution and

(ii) the number of milli moles of HCl in 100 ml of the final solution.

**Ans.** (i) 0.569 M (ii) 56.9

**Sol.** Mol. wt. of HCl = 36.5

$$\text{Mass of HCl in 1L of } \frac{\text{M}}{2} \text{ HCl} = \frac{1}{2} \times 36.5 = 18.25 \text{ g}$$

Weight of HCl lost on heating = 2.675 g

Weight of HCl left in solution =  $18.25 - 2.675 = 15.575 \text{ g}$

$$\text{Number of moles in 15.575 g HCl} = \frac{15.575}{36.5} = 0.4267$$

$$\text{Volume of the solution left after heating} = 750 \text{ ml} = \frac{750}{1000} = 0.75 \text{ L}$$

$$\therefore \text{Molarity of solution} = \frac{\text{No. of gram moles}}{\text{Volume in litres}} = \frac{0.4267}{0.75} = 0.569 \text{ M}$$

Now number of milli moles = (volume in ml)  $\times$  (Molarity)

$$= 100 \times 0.569 = 56.9$$

**Q.38** Calculate the normality of a solution obtained by mixing 0.01 L of  $\frac{\text{N}}{10}$  NaOH and 40 ml of seminormal KOH solution.

**Ans.** 0.42 N

**Sol.** Total volume (V) of mixed solution =  $\left(0.01 \text{ L} \times \frac{1000 \text{ mL}}{1 \text{ L}}\right) + 40 \text{ ml} = 50 \text{ ml}$

Now  $N_1 V_1 + N_2 V_2 = NV$

$$\frac{1}{10} \times 10 + \frac{1}{2} \times 40 = N \times 50$$

$$\therefore N = \frac{21}{50} = 0.42 \text{ geq L}^{-1}$$



**Q.39** 30 ml  $\text{Na}_2\text{CO}_3$  solution is mixed in 20 ml 0.8 N  $\text{H}_2\text{SO}_4$ . The resulting solution required 20 ml 0.7 N HCl for neutralization. Calculate the strength of  $\text{Na}_2\text{CO}_3$  solution in g/L, Take  $\text{Na}_2\text{CO}_3$  as anhydrous.

**Ans.** 53 g/L

**Sol.** meq of acids =  $(20 \times 0.8) + (20 \times 0.7) = 16 + 14 = 30$   
meq of  $\text{Na}_2\text{CO}_3 = 30$

$$\text{Normality of } \text{Na}_2\text{CO}_3 = \frac{30}{30} = 1\text{N}$$

$$\text{Strength} = N \times \text{eq. wt} = \left(1 \times \frac{106}{2}\right) = 53 \text{ g/L}$$

**Q.40** 1 g sample of  $\text{H}_2\text{O}_2$  solution containing x % of  $\text{H}_2\text{O}_2$  by weight requires x ml  $\text{KMnO}_4$  solution for complete oxidation under acidic conditions. Calculate the normality of  $\text{KMnO}_4$  solution.

**Ans.** 0.588 N

**Sol.** 1 g of solution contains  $\frac{1 \times x}{100} = 0.01 \times \text{g } \text{H}_2\text{O}_2$

17 g (eq. wt.) of  $\text{H}_2\text{O}_2$  is present in 1000 ml 1N solution

$\therefore 0.01 \times \text{g (eq. wt.) of } \text{H}_2\text{O}_2$  is present in  $\frac{1000 \times 0.01x}{17}$  ml 1N solution

$$\text{Now, } \frac{1000 \times 0.01x}{17} \times N = x \times N_{\text{KMnO}_4}$$

$$N_{\text{KMnO}_4} = \frac{1000 \times 0.01x \times N}{17 \times x} = 0.588 \text{ N}$$

# CHEMICAL BONDING

## INTRODUCTION

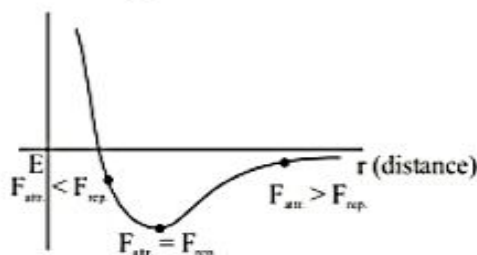
- (i) Most of the elements exist as molecules which are cluster of atoms. How do atoms combine to form molecules and why do atoms form bonds. Such doubts will be discussed in this chapter.
- (ii) A molecule will only be formed if it is more stable and has a lower energy, than the individual atoms.

## CHEMICAL BOND

- (i) A force that acts between two or more atoms to hold them together as a stable molecule.
- (ii) It is union of two or more atoms involving redistribution of electron among them.
- (iii) This process accompanied by decrease in energy.
- (iv) Decrease in energy  $\propto$  Strength of the bond.
- (v) Therefore molecules are more stable than atoms.

### Cause of Chemical Combination

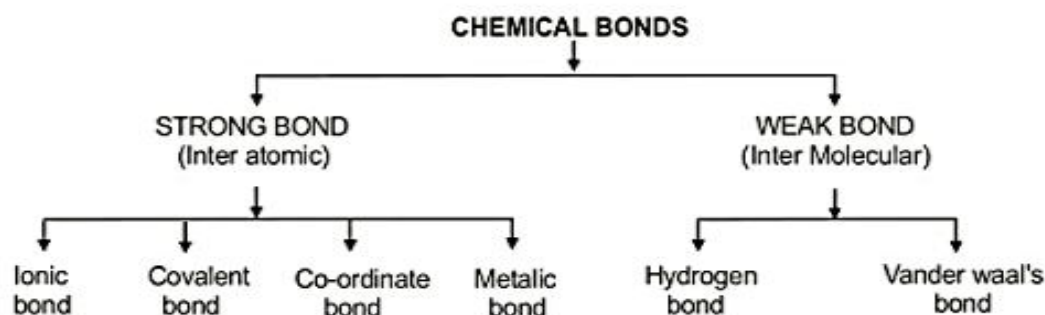
#### 1. Tendency to acquire minimum energy :



- (i) When two atoms approaches to each other. Nucleus of one atom attracts the electron of another atom.
- (ii) According to quantum theory when two atoms of element approach each other then there will be force of attraction as well as force of repulsion between the bonded atoms. At the minimum distance where these forces becomes equal is called bond formation condition (equilibrium state) and atom of the elements get stabilized by bond formation phenomena by lowering their energy.
- (iii) If net result is attraction, the total energy of the system (molecule) decreases and a chemical bond forms.
- (iv) **So, Attraction  $\propto$  1/energy  $\propto$  Stability.**
- (v) Bond formation is an exothermic process

#### 2. Tendency to acquire noble gas configuration :

- (i) Atom combines to acquire noble gas configuration.
- (ii) Only outermost electron i.e. ns, np and (n-1)d electrons participate in bond formation.
- (iii) Inert gas elements do not participate, as they have stable electronic configuration and hence minimum energy. (Stable electronic configuration :  $1s^2$  or  $ns^2np^6$ )



### Lewis Octet Rule

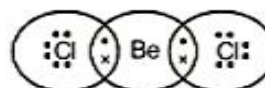
- (i) Every atom has a tendency to complete its octet.
- (ii) Hydrogen has the tendency to complete its duplet.
- (iii) To acquire inert gas configuration atoms lose or gain electron or share electron.
- (iv) The tendency of atoms to achieve eight electrons in their outer most shell is known as Lewis octet rule.

e.g.,  $\text{H}_2\text{O}$  molecule



Obeys octet rule

e.g.,  $\text{BeCl}_2$  Molecule



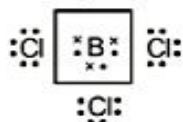
Doesn't obeys octet rule

### Exception of Octet Rule :

- (a) **Incomplete octet molecules : or (electron deficient molecules) or Hypovalent molecules**

Compound in which octet is not complete in outer most orbit of central atom.

Examples - Halides of IIIA groups,  $\text{BF}_3$ ,  $\text{AlCl}_3$ ,  $\text{BCl}_3$ , hydride of III A/ $13^{\text{th}}$  group etc.



{ In  $\text{BCl}_3$   
Boron has only 6 electrons }

Other examples -  $\text{BeCl}_2$  (4 electron),  $\text{ZnCl}_2$  (4 electron),  $\text{Ga}(\text{CH}_3)_3$  (6 electron)

- (b) **Expansion of octet or (electron efficient molecules) or Hypervalent molecules**

Compound in which central atom has more than 8 electron in outermost orbits.

Example -  $\text{PCl}_5$ ,  $\text{SF}_6$ ,  $\text{IF}_7$ , the central atom P, S and I contain 10, 12, and 14 electrons respectively.



Electron dot formula of  $\text{PCl}_5$

- (c) **Pseudo inert gas configuration : -**

**Cations of transition metals, which contains 18 electrons in outermost orbit**

Examples :  $\text{Ga}^{+3}$ ,  $\text{Cu}^+$ ,  $\text{Ag}^+$ ,  $\text{Zn}^{+2}$ ,  $\text{Cd}^{+2}$ ,  $\text{Sn}^{+4}$ ,  $\text{Pb}^{+4}$  etc.

Electronic configuration of Ga -  $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^1$

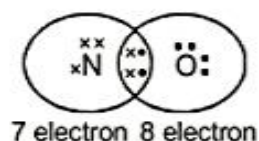
Electronic configuration of  $\text{Ga}^{+3}$  -  $1s^2, 2s^2 2p^6, \underline{3s^2 3p^6 3d^{10}}$   
18 electron

**(d) Odd electron molecules : -**

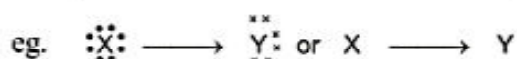
Central atom have an unpaired electron or odd number (7 electron, 11 electron, etc) of electrons in their outer most shell.

Examples : NO, NO<sub>2</sub>, ClO<sub>2</sub>, ClO<sub>3</sub> etc.

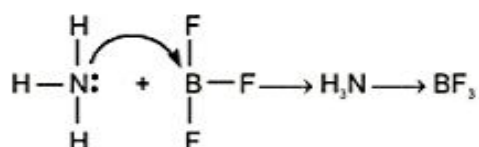
e.g., NO molecule

**CO-ORDINATE BOND (DATIVE BOND)**

- (i) It is a covalent bond in which the shared electron pair come from one atom is called coordinate bond.
- (ii) Necessary conditions for the formation of co-ordinate bond are-
  - (a) Octet of donor atom should be complete and should have atleast one lone pair of electron.
  - (b) Acceptor atom should have a deficiency of at least one pair of electron.

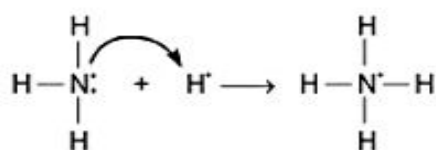


- (iii) Atom which provide electron pair for sharing is called donor.
- (iv) Other atom which accepts electron pair is called acceptor. That is why it is called donor-acceptor or dative bond



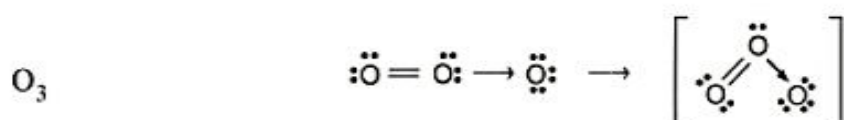
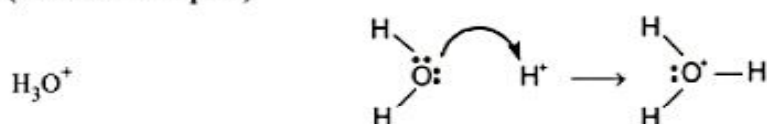
BF<sub>3</sub> is electron deficient compound.

Example: NH<sub>4</sub><sup>+</sup>



(Bronsted - Lowry acid)

(electron acceptor)





# IMPORTANT LEWIS ELECTRON DOT/CROSS STRUCTURES

	Compound	Structure	Electron dot/Cross formula
1.	Sodium Sulphide ( $\text{Na}_2\text{S}$ )	$2(\text{Na}^+)\text{S}^{--}$	$\text{Na}^+ \text{:}\ddot{\text{S}}\text{:}^\ominus \text{Na}^+$
2.	Calcium Hydride ( $\text{CaH}_2$ )	$\text{Ca}^{++}2(\text{H}^-)$	$\text{H:} \text{Ca}^{++} \text{H:}$
3.	Hydrogen Peroxide ( $\text{H}_2\text{O}_2$ )	$\text{H}-\text{O}-\text{O}-\text{H}$	$\text{H:}\ddot{\text{O}}\text{:}\ddot{\text{O}}\text{:H}$
4.	Phosphine ( $\text{PH}_3$ )	$\begin{array}{c} \text{H} \\   \\ \text{H}-\text{P}-\text{H} \end{array}$	$\begin{array}{c} \text{H} \\   \\ \text{H:}\ddot{\text{P}}\text{:H} \end{array}$
5.	Carbon mono-oxide ( $\text{CO}$ )	$\text{C}\equiv\text{O}$	$\text{:C}\text{:}\ddot{\text{O}}\text{:}$
6.	Carbon di-oxide ( $\text{CO}_2$ )	$\text{O}=\text{C}=\text{O}$	$\ddot{\text{O}}\text{:}\ddot{\text{C}}\text{:}\ddot{\text{O}}$
7.	Hydrogen Cyanide ( $\text{HCN}$ )	$\text{H}-\text{C}\equiv\text{N}$	$\text{H:}\text{C}\text{:}\ddot{\text{N}}\text{:}$
8.	Potassium Isocyanide ( $\text{KNC}$ )	$\text{K}^+ \text{N}\equiv\text{C}$	$\text{K}^+ [\text{N}\text{:}\ddot{\text{C}}\text{:}]^-$
9.	Sodium Hydroxide ( $\text{NaOH}$ )	$\text{Na}^+ \text{O}^--\text{H}$	$\text{Na}^+ [\text{:}\ddot{\text{O}}\text{:H}]^-$
10.	Nitrous oxide ( $\text{N}_2\text{O}$ )	$\text{N}\equiv\text{N}\rightarrow\text{O}$	$\text{:N}\text{:}\ddot{\text{N}}\text{:}\ddot{\text{O}}\text{:}$
11.	Nitric oxide ( $\text{NO}$ or $\text{N}_2\text{O}_2$ )	$\text{O}=\text{N}-\text{N}=\text{O}$	$\ddot{\text{O}}\text{:}\ddot{\text{N}}\text{:}\ddot{\text{N}}\text{:}\ddot{\text{O}}$
12.	Dinitrogen tri oxide ( $\text{N}_2\text{O}_3$ )	$\begin{array}{c} \text{O} \\   \\ \text{O}=\text{N}-\text{N}=\text{O} \end{array}$	$\begin{array}{c} \ddot{\text{O}}\text{:} \\   \\ \ddot{\text{O}}\text{:}\ddot{\text{N}}\text{:}\ddot{\text{N}}\text{:}\ddot{\text{O}} \end{array}$
13.	Dinitrogen tetraoxide ( $\text{N}_2\text{O}_4$ )	$\begin{array}{c} \text{O} \quad \text{O} \\   \quad   \\ \text{O}=\text{N}-\text{N}=\text{O} \end{array}$	$\begin{array}{c} \ddot{\text{O}}\text{:} \quad \ddot{\text{O}}\text{:} \\   \quad   \\ \ddot{\text{O}}\text{:}\ddot{\text{N}}\text{:}\ddot{\text{N}}\text{:}\ddot{\text{O}} \end{array}$
14.	Nitrogen Penta oxide ( $\text{N}_2\text{O}_5$ )	$\begin{array}{c} \text{O} \quad \text{O} \\   \quad   \\ \text{O}=\text{N}-\text{O}-\text{N}=\text{O} \end{array}$	$\begin{array}{c} \ddot{\text{O}}\text{:} \quad \ddot{\text{O}}\text{:} \\   \quad   \\ \ddot{\text{O}}\text{:}\ddot{\text{N}}\text{:}\ddot{\text{O}}\text{:}\ddot{\text{N}}\text{:}\ddot{\text{O}} \end{array}$
15.	Nitrous acid ( $\text{HNO}_2$ )	$\text{H}-\text{O}-\text{N}=\text{O}$	$\text{H:}\ddot{\text{O}}\text{:}\ddot{\text{N}}\text{:}\ddot{\text{O}}$
16.	Nitric acid ( $\text{HNO}_3$ )	$\begin{array}{c} \text{O} \\   \\ \text{H}-\text{O}-\text{N}=\text{O} \end{array}$	$\begin{array}{c} \ddot{\text{O}}\text{:} \\   \\ \text{H:}\ddot{\text{O}}\text{:}\ddot{\text{N}}\text{:}\ddot{\text{O}} \end{array}$



17.	Nitrate Ion ( $\text{NO}_3^-$ )	$\text{O} \leftarrow \text{N} = \text{O}^-$	$\left[ \begin{array}{c} :\ddot{\text{O}}: \\ :\ddot{\text{O}}: \text{N} : \ddot{\text{O}}: \end{array} \right]^-$
18.	Ammonium Chloride ( $\text{NH}_4\text{Cl}$ )	$\left[ \begin{array}{c} \text{H} \\   \\ \text{H}-\text{N}-\text{H} \\   \\ \text{H} \end{array} \right]^+ \text{Cl}^-$	$\left[ \begin{array}{c} \text{H} \\   \\ \text{H} \cdots \text{N} \cdots \text{H} \\   \\ \text{H} \end{array} \right]^+ :\ddot{\text{Cl}}^-$
19.	Carbonate Ion ( $\text{CO}_3^{--}$ )	$\text{O}^- - \text{C} = \text{O}$	$\left[ \begin{array}{c} :\text{O}: \\ :\ddot{\text{O}}: \text{C} : \ddot{\text{O}}: \end{array} \right]^{-2}$
20.	Sulphur di-oxide ( $\text{SO}_2$ )	$\text{O} \leftarrow \text{S} = \text{O}$	$:\ddot{\text{O}}: \ddot{\text{S}} :: \ddot{\text{O}}$
21.	Sulphur Tri-oxide ( $\text{SO}_3$ )	$\text{O} \leftarrow \text{S} = \text{O}$	$:\ddot{\text{O}}: \ddot{\text{S}} :: \ddot{\text{O}}$
22.	Sulphite Ion ( $\text{SO}_3^{--}$ )	$\text{O}^- - \text{S} = \text{O}$	$\left[ \begin{array}{c} :\ddot{\text{O}}: \\ :\ddot{\text{O}}: \text{S} : \ddot{\text{O}}: \end{array} \right]^{-2}$
23.	Sulphate Ion ( $\text{SO}_4^{--}$ )	$\text{O}^- - \text{S} = \text{O}$	$\left[ \begin{array}{c} :\ddot{\text{O}}: \\ :\ddot{\text{O}}: \text{S} : \ddot{\text{O}}: \\ :\text{O}: \end{array} \right]^{-2}$
24.	Thio-sulphate Ion ( $\text{S}_2\text{O}_3^{--}$ )	$\text{O}^- - \text{S} = \text{O}$	$\left[ \begin{array}{c} :\ddot{\text{S}}: \\ :\ddot{\text{O}}: \text{S} : \ddot{\text{O}}: \\ :\text{O}: \end{array} \right]^{-2}$
25.	Phosphoric Acid ( $\text{H}_3\text{PO}_4$ )	$\begin{array}{c} \text{H} \\   \\ \text{H}-\text{O}-\text{P}-\text{O}-\text{H} \\   \\ \text{O} \end{array}$	$\begin{array}{c} \text{H} \\   \\ :\text{O}: \\ \text{H} :: \ddot{\text{O}}: \text{P} : \ddot{\text{O}} :: \text{H} \\   \\ :\text{O}: \end{array}$

26.	Phosphorous acid ( $\text{H}_3\text{PO}_3$ )	$\begin{array}{c} \text{H} \\   \\ \text{H}-\text{O}-\text{P}-\text{O}-\text{H} \\   \\ \text{O} \end{array}$	$\begin{array}{c} \text{H} \\ \vdots \\ \text{H}::\ddot{\text{O}}::\text{P}::\ddot{\text{O}}::\text{H} \\ \vdots \\ \text{O} \end{array}$
27.	Phosphate Ion ( $\text{PO}_4^{3-}$ )	$\begin{array}{c} \ominus \\   \\ \text{O}-\text{P}-\text{O} \\   \\ \text{O} \end{array}$	$\left[ \begin{array}{c} \ddot{\text{O}} \\ \vdots \\ \ddot{\text{O}}::\text{P}::\ddot{\text{O}} \\ \vdots \\ \ddot{\text{O}} \end{array} \right]^{-}$
28.	Potassium Permanganate ( $\text{KMnO}_4$ )	$\text{K}^+ \left[ \begin{array}{c} \text{O} \\ \updownarrow \\ \text{O} \leftarrow \text{Mn} \rightarrow \text{O} \\ \downarrow \\ \text{O} \end{array} \right]^{-}$	$\left[ \begin{array}{c} \ddot{\text{O}} \\ \vdots \\ \ddot{\text{O}}::\text{Mn}::\ddot{\text{O}} \\ \vdots \\ \ddot{\text{O}} \end{array} \right]^{-}$

**Illustration**

1. Which of the following species are hypervalent?

1.  $\text{ClO}_4^-$ , 2.  $\text{BF}_3$ , 3.  $\text{SO}_4^{2-}$ , 4.  $\text{CO}_3^{2-}$

(A) 1, 2, 3

(B) 1, 3

(C) 3, 4

(D) 1, 2

Ans. (B)

Sol. Hypervalent : Central atom of the compound having more than  $8e^-$ .

**Exercise**

1. The octet rule is not obeyed in :

(A)  $\text{CO}_2$

(B)  $\text{BCl}_3$

(C)  $\text{PCl}_5$

(D)  $\text{SiF}_4$

Ans. (B), (C)

2. To which of the following species octet rule is not applicable :

(A)  $\text{BrF}_5$

(B)  $\text{SF}_6$

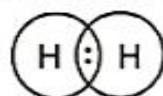
(C)  $\text{IF}_7$

(D)  $\text{CO}$

Ans. (A), (B), (C)

**COVALENT BOND**

- (i) A covalent bond is formed by the mutual sharing of electrons between two atoms to complete their octet. (Except H which completes its duplet).



H—H  
 $\text{H}_2$  molecule



O=O  
 $\text{O}_2$  molecule



N≡N  
 $\text{N}_2$  molecule

- (ii) The shared pair of electrons should have opposite spins, and are localised between two atoms concerned.

(iii) Shairing of electrons may occurs in three ways –

No. of electrons shared between two atoms	Electron pair	Bond
2	1	Single bond (—)
4	2	Double bond (=)
6	3	Triple bond (≡)

Examples –  $\text{H}-\ddot{\text{N}}-\text{H}$  Three single bonds (not triple bond)

$\ddot{\text{N}} \equiv \ddot{\text{N}}$ , Triple bond. (not three single bond)

$\ddot{\text{O}} = \ddot{\text{O}}$ , Double bond (Not two single bond)

$\text{H}-\ddot{\text{O}}-\text{H}$ , (Two single bonds.)

### Orbital concept of covalent bond :

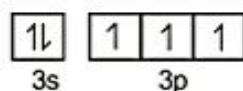
- One orbital can accomodate at the most 2 electrons with opposite spins  $\uparrow\downarrow$
- Half filled orbital or unpaired electron orbital accepts one electron from another atom, to complete its orbitals.
- Tendency to complete orbital or to pair the electron is an essential condition of covalent bond. Completion of octet is not the essential condition of covalent bond.
- Covalency** : It is defined as the number of electrons contributed by an atom of the element for shairing with other atoms to achieve noble gas configuration.
- If the outermost orbit has empty orbitals then covalent bonds are formed in excited state.

### Variable valency in covalent bonds :

- Variable valencies are shown by those elements which have empty orbitals in outermost shell.
- Lone pair electrons gets excited in the subshell of the same shell to form the maximum number of unpaired electrons. Maximum covalency is shown in excited state.
- The energy required for excitation of electrons is called promotion energy.
- Promotion rule – Excitation of electrons in the same orbit.

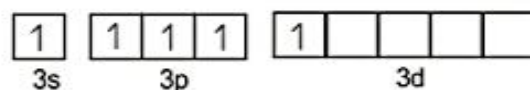
### Example :

(a) Phosphorus → Ground state



Covalency 3 ( $\text{PCl}_3$ )

Phosphorus → Excited state



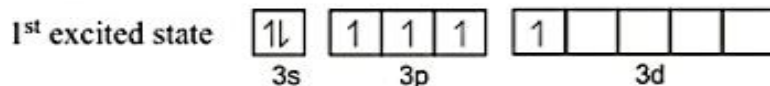
Covalency – 5 ( $\text{PCl}_5$ )

(b) Sulphur → Ground state.

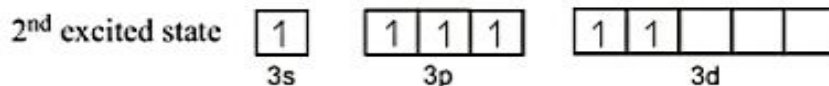


Covalency – 2 ( $\text{SF}_2$ )

Sulphur → Excited state



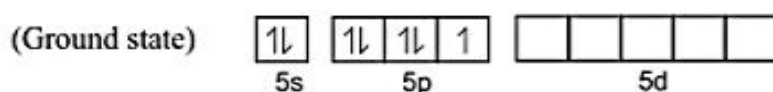
Covalency – 4 ( $\text{SF}_4$ )



Covalency – 6 ( $\text{SF}_6$ )

So variable covalency of S is 2, 4 & 6.

(c) Iodine has three lone pair of electrons



So it shows three excited states – Maximum number of unpaired electrons = 7

Variable Valencies are 1, 3, 5, 7

### Applications of Variable Valency :

**To explain existence of molecules :**

$\text{NCl}_3$  – exists

$\text{NCl}_5$  – doesn't exist (due to absence of d-orbitals in Nitrogen.) While  $\text{PCl}_3$  and  $\text{PCl}_5$  both exist because 3d orbitals are present in phosphorus.

$\text{OF}_2$  — exists, but  $\text{OF}_4$  and  $\text{OF}_6$  doesn't exist due to absence of d-orbitals, while  $\text{SF}_4$  and  $\text{SF}_6$  exist due to presence of d-orbital, present in its valence shell.

**Note :** Compound in which Ionic, covalent and co-ordinate bonds are present are following

$\text{NH}_4\text{Cl}$ ,  $\text{CuSO}_4$ ,  $\text{K}_4[\text{Fe}(\text{CN})_6]$ ,  $\text{KNC}$ ,  $\text{Na}_3\text{PO}_4$ ,  $\text{KNO}_3$ , etc.

### Wave mechanical concept of chemical bonding – (Overlapping)

To explain the nature of covalent bond two theories based on quantum mechanics have been proposed.

(1) Valence bond theory (VBT)

(2) Molecular orbital theory (MOT)

## VALENCE BOND THEORY

- (i) It was presented by Heitler & London to explain how a covalent bond is formed. It was extended by Pauling & Slater.
- (ii) The main points of theory are –
  - (a) To form a covalent bond overlapping occurs between half filled valence shell orbitals of the two atoms.
  - (b) Resulting bond acquires a pair of electrons with opposite spins to get stability.
  - (c) Orbitals come closer to each other from the direction in which there is maximum overlapping
  - (d) So covalent bond has directional character.
  - (e) Extent of overlapping  $\propto$  strength of chemical bond.



(f) Extent of overlapping depends on two factors.

(i) Nature of orbitals – p, d and f are directional orbitals → more overlapping  
s-orbitals → non directional – less overlapping

(ii) Nature of overlapping – Co-axial overlapping - extent of overlapping more.  
Collateral overlapping - extent of overlapping less

Order of strength of Co - axial overlapping –

$$p - p > s - p > s - s$$



(g) As the value of n increases, bond strength decreases.

$$1 - 1 > 1 - 2 > 2 - 2 > 2 - 3 > 3 - 3$$

(h) If n is same bond strength order will be following

$$2p - 2p > 2s - 2p > 2s - 2s$$

$$1s - 2p > 2s - 2p > 3s - 3p$$

(i) Electron which is already paired in valency shell can enter into bond formation, if they can be unpaired first and shifted to vacant orbitals of slightly higher energy of the same energy shell.

(j) This point can explain the trivalency of boron, tetravalency of carbon, penta-valency of phosphorus etc.

(k) Two types of bonds are formed on account of overlapping.

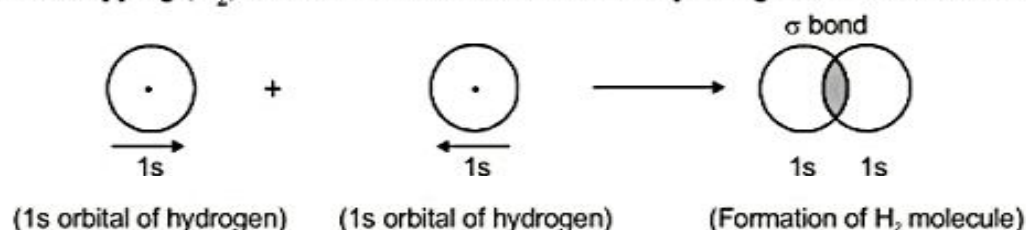
(A) Sigma ( $\sigma$ ) bond      (B) Pi ( $\pi$ ) bond

#### (A) Sigma ( $\sigma$ ) bond :

- (i) Bond formed between two atoms by the overlapping of half filled orbitals along their axis (end to end overlap) is called sigma bond.
- (ii)  $\sigma$  bond do not take part in resonance.
- (iii) Free rotation is possible about a single  $\sigma$  bond.
- (iv) Maximum overlapping is possible between electron clouds and hence it is strong bond.
- (v) There can be only  $\sigma$  bond between two atoms.

Sigma bond are formed by four types of overlapping

(a) s - s overlapping ( $H_2$ ) - Two half filled s-orbitals overlap along the internuclear axis.

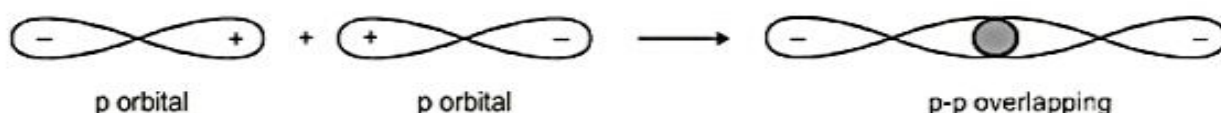


(b) s - p overlapping (Formation of HF) – When half fill s-orbital of one atom overlap with half filled p-orbital of other atom.



- (c) p-p overlapping – (Coaxial) – It involves the coaxial overlapping between half filled p-orbitals of two different atoms.

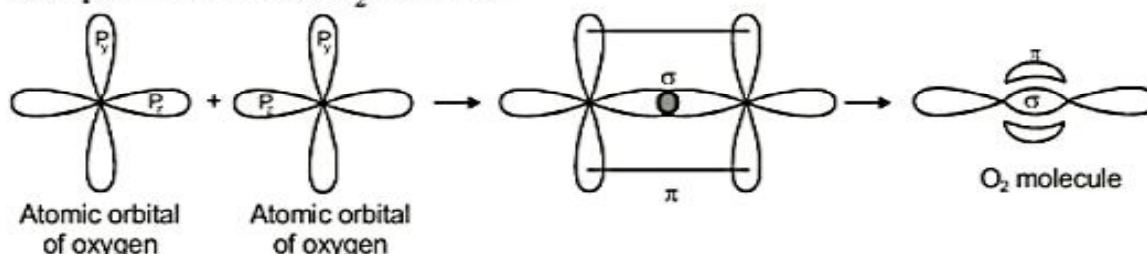
eg. Formation of  $\text{Cl}_2$ ,  $\text{F}_2$ ,  $\text{Br}_2$



### (B) Pi ( $\pi$ ) bond

- (i) The bond formed by sidewise (lateral) overlapping are known as  $\pi$  bonds.
- (ii) Lateral overlapping is only partial, so bonds formed are weaker and hence more reactive than  $\sigma$  bonds (Repulsion between nucleus is more as orbitals have to come much close to each other for  $\pi$  bond formation)

Example – Formation of  $\text{O}_2$  molecule –



Only  $p_y$  and  $p_z$  of oxygen atom have unpaired electron in each orbital for bonding.

Electronic configuration of oxygen is –  $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$

- (iii) Free rotation about a  $\pi$  bond is not possible.
- (iv)  $\pi$  bond is weaker than  $\sigma$  bond (Bond energy difference is 63.5 KJ or 15 K cal/mole)
- (v)  $\pi$  bond takes part in resonance.
- (vi)  $\pi$  bond formed by pure or unhybrid orbitals.

### Illustration

1. When  $2s-2s$ ,  $2p-2p$  and  $2p-2s$  orbitals overlap, the bond strength decreases in the order :  
(A)  $p-p > s-s > p-s$  (B)  $p-p > p-s > s-s$  (C)  $s-s > p-p > p-s$  (D)  $s-s > p-s > p-p$

Ans. (B)

Sol. Bond strength  $\propto$  directional property of orbitals.

### Exercise

1. Which of the following has been arranged in order of decreasing bond length ?  
(A)  $P-O > Cl-O > S-O$  (B)  $P-O > S-O > Cl-O$   
(C)  $S-O > Cl-O > P-O$  (D)  $Cl-O > S-O > P-O$

Ans. (B)

2. A  $\pi$ -bond may be formed between two  $p_x$  orbitals containing one unpaired electron each when they approach each other appropriately along :

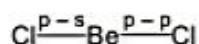
(A) x - axis                      (B) y - axis                      (C) z - axis                      (D) B & C

Ans. (D)

## HYBRIDISATION

Consider an example of Be compound :-

If it is formed without hybridisation then -



both the Be-Cl bonds should have different parameters and p-p bond strength is greater than s-p bond strength.

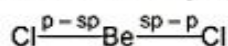
Practically bond strength and distance of both the Be-Cl bonds are same.

This problem may overcome if hybridisation of s and p-orbital occurs.

### Hybridisation :

- (i) It is introduced by Pauling, to explain equivalent nature of covalent bonds in a molecule.
- (ii) **Definition :** Mixing of different shapes and approximate equal energy atomic orbitals, and redistribution of energy to form new orbitals, of same shape & same energy. These new orbitals are called hybrid orbitals and the phenomenon is called hybridisation.

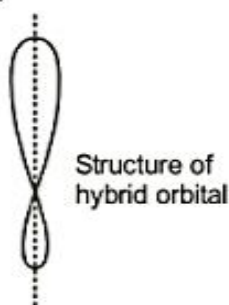
Now after considering s-p hybridisation in  $\text{BeCl}_2$



bond strength of both the bonds will be equal.

### Characteristic of Hybridisation :

- (i) Hybridisation is a mixing of orbitals and not electrons. Therefore in hybridisation full filled, half filled and empty orbitals may take part.
- (ii) Number of the hybrid orbitals formed is always be equivalent to number of atomic orbital which have taken part in the process of hybridisation.



- (iii) Each hybrid orbital having two lobes, one is larger and other is smaller. Bond will be formed from large lobe.
- (iv) The number of hybrid orbitals on central atom of a molecule or ion = number of  $\sigma$  bonds + lone pair of electron.
  - (a) The 1<sup>st</sup> bond between two atoms will be sigma.
  - (b) The other bond between same two atoms will be  $\pi$  bond.
  - (c) The electron pair of an atom which do not take part in bond formation called as lone pair of electron.
- (v) One element can represent many hybridisation state depending on experimental conditions for example, Carbon showing  $sp$ ,  $sp^2$  and  $sp^3$  hybridisation in its compounds.
- (vi) Hybrid orbitals are differentiated as  $sp$ ,  $sp^2$ ,  $sp^3$  etc.



- (vii) The order of repulsion between  $\ell p$  &  $bp$  is :  $\ell p - \ell p > \ell p - bp > bp - bp$
- (viii) The directional properties in hybrid orbital is more than atomic orbitals. Therefore hybrid orbitals form stronger sigma bond. The directional property of different hybrid orbitals will be in following order.

$$sp < sp^2 < sp^3 < sp^3d < sp^2d^2 < sp^3d^3$$

### Difference between hybridisation & overlapping

Overlapping	Hybridisation
1. It occurs between orbitals of two atoms	1. It occurs among orbitals of the same atom
2. Only half filled orbitals takes part in overlapping	2. Any type of orbital can participates
3. It occurs during bond formation bond formed after hybridisation	3. Process, just before overlapping.
4. Orbital of different energies may participates in excited states.	4. It may takes place in ground or in excited state In ground state– $NH_3$ , $NCl_3$ , $PH_3$ , $PCl_3$ ,

### Determination of hybridisation state :

#### Method (I) :

Count the following pair of electron around the central atom :

- Count all pure  $\sigma$  bonded electron pairs (or  $\sigma$  bonds)
- Count all lone pair of electron
- Count Co-ordinate bond

#### Method (II) :

To predict hybridisation following formula may be used :

Number of hybrid orbital =  $\frac{1}{2}$  [Total number of valence electron in the central atom + total number of monovalent atoms – charge on cation + charge on anion]

eg.  $NH_4^+$  :  $H = \frac{1}{2}[5 + 4 - 1] = 4$  :  $sp^3$  hybridisation.

$SF_4$  :  $H = \frac{1}{2}[6 + 4] = 5$  :  $sp^3d$  hybridisation.

$SO_4^{2-}$  :  $H = \frac{1}{2}[6 + 2] = 4$  :  $sp^3$  hybridisation.

(‘O’ is divalent so add only charge on anion)

$NO_3^-$  :  $H = \frac{1}{2}[5 + 1] = 3$  :  $sp^2$  hybridisation.



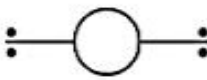
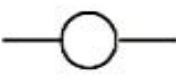
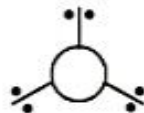


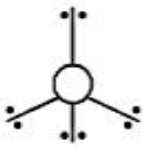



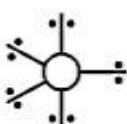

Where,  $H$  is the number of hybrid orbitals.

If such type of electron pairs are –

two	–	$sp$	hybridisation
three	–	$sp^2$	hybridisation
four	–	$sp^3$	hybridisation
five	–	$sp^3d$	hybridisation
six	–	$sp^3d^2$	hybridisation
seven	–	$sp^3d^3$	hybridisation

### Shape of covalent molecules :

– It was given by Sidgwick & Powell.

No. of electron pair	electronic geometry	$\ell.p.$	b.p.	Shape of molecule	Example
2		0	2	 linear	$BeCl_2$ , $CO_2$
3		0	3	 trigonal planar	$BF_3$ , $BCl_3$
		1	2	 V/bent/angular shape	$SnCl_2$
4		0	4	 tetrahedral	$CH_4$
		1	3	 trigonal pyramidal	$NH_3$
		2	2	 V/bent/angular	$H_2O$
5		0	5	 trigonal bipyramidal	$PCl_5$

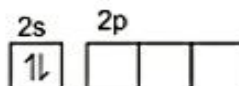
6		1	4		SF <sub>4</sub>
		3	2		ClF <sub>3</sub>
		2	3		XeF <sub>2</sub>
		0	6		SF <sub>6</sub>
		1	5		BrF <sub>5</sub>
		2	4		XeF <sub>4</sub>

### Types of Hybridisation :

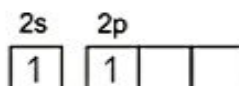
#### sp hybridisation :

- In this hybridisation one s-orbital & one p-orbital of an atom are mixed to give two new hybrid orbitals which are equivalent in shape & energy known as sp hybrid orbitals.
- These two sp hybrid orbitals are arranged in a straight line & 180° bond angle.
- % s-character is 50%

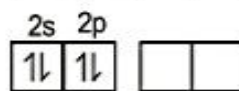
Be (ground state)



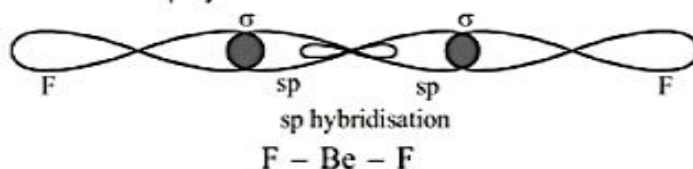
Be (excited state)



Be atom accepts two electrons from F in BeF<sub>2</sub>,

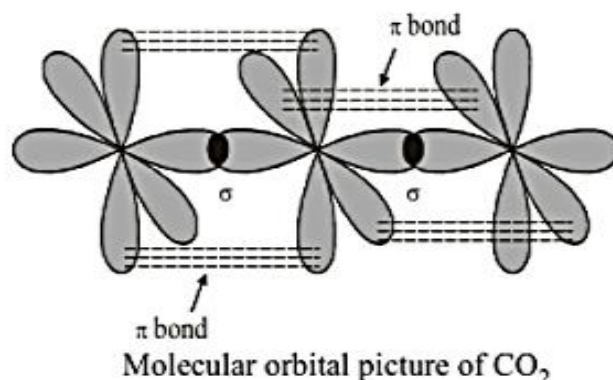


two sp hybridisation

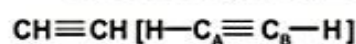


### CO<sub>2</sub> Molecule (O = C = O) :

In CO<sub>2</sub> molecule, C has two sp hybrid orbitals & two unhybridised p orbitals.

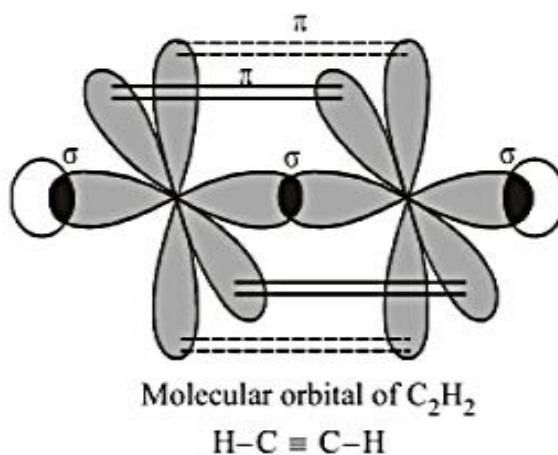


- Thus, CO<sub>2</sub> molecule is a linear in shape & having 180° bond angle.
- The bond length between C–O bond is reduced due to the presence of π bond.



In CH≡CH molecules, each C atom contains two sp hybrid orbitals & two unhybridised p orbitals

	2s	2p
C(ground state)	$\uparrow\downarrow$	$\uparrow$ $\uparrow$ $\square$
C(excited state)	$\uparrow$	$\uparrow$ $\uparrow$ $\uparrow$
C atom accepts two electrons from H & C, In C <sub>2</sub> H <sub>2</sub>	$\uparrow\downarrow$ $\uparrow\downarrow$	$\uparrow$ $\uparrow$
	two sp hybridisation	



sp hybrid orbital of each C atom overlaps to give sigma bond between C – C.

The remaining one sp hybrid orbital of each C atom overlaps with s orbital of H, forming sigma bond between C – H.

The two unhybridised p orbitals of each C atom (p<sub>y</sub> and p<sub>x</sub>) overlap laterally to form two pi(π) bonds.

Therefore in H–C<sub>A</sub> ≡ C<sub>B</sub>–H

sigma bond between  $C_A - C_B$  is formed  $sp - sp$  overlapping

sigma bond between  $C_A - H$  is formed  $sp - s$  overlapping

sigma bond between  $C_B - H$  is formed  $sp - s$  overlapping

pi bond between  $C_A - C_B$  is formed :  $p_y - p_y, p_x - p_x$  overlapping

Each C atom forms two sigma bonds but in  $C_2H_2$ , total sigma bonds are 3

Each C atom forms two  $\pi$  bonds. Total  $\pi$  bonds in  $C_2H_2$  are two

Total number of bonds in acetylene are :

$$3\sigma + 2\pi \text{ bond} = 5 \text{ bonds}$$

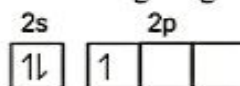
### Examples on $sp$ hybridisation

Example	$\sigma$ bond	Lone pair electrons	Hybridisation	Bond angle	Shape
$BeH_2, BeCl_2$ $CO_2, NO_2^+, C_2H_2$ $,HCN, HgCl_2, N_2O,$ $N_3^-$	2	0	$sp$	$180^\circ$	Linear

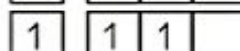
### $sp^2$ Hybridisation :

- In this hybridisation one  $s$  & two  $p$  orbitals are mixed to give three new  $sp^2$  hybrid orbitals which all are in the same shape & equivalent energies.
- These three  $sp^2$  hybrid orbitals are at angle of  $120^\circ$  & giving **trigonal planar shape**.

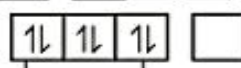
B (ground state)



B (excited state)

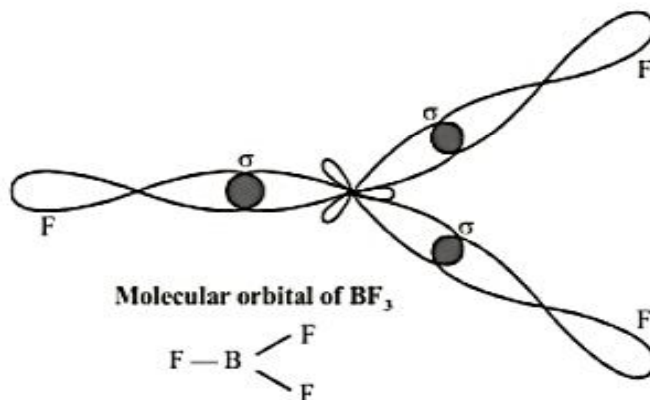


B atom accepts 3 electrons



three  $sp^2$  hybrid orbitals

From 3 F atom  $\therefore$  in  $BF_3$



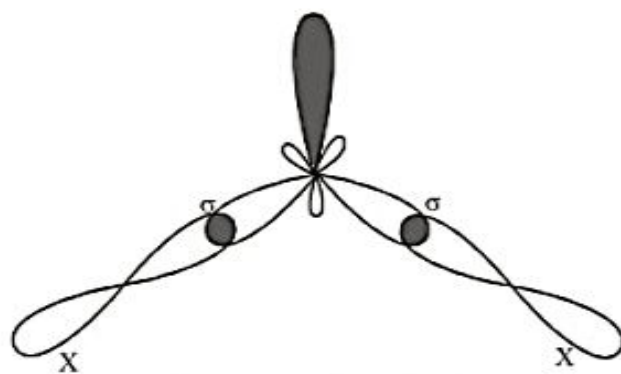
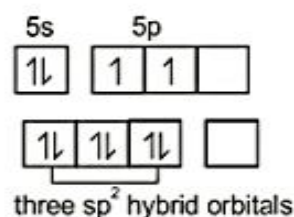
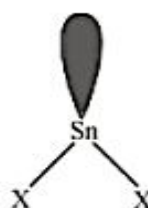
- %  $s$  - character = 33.3%



**SnX<sub>2</sub> (X = F, Cl, Br, I)**

Sn (ground state)

Sn after hybridisation shares two electron with two atom.


**Molecular orbital of SnX<sub>2</sub>**

 SnX<sub>2</sub> having two  $\sigma$  bonds & one lone pair electron, therefore, hybridisation is sp<sup>2</sup>

 The bond angle in SnX<sub>2</sub> will be less than 120° (due to presence of one lone pair electrons.)

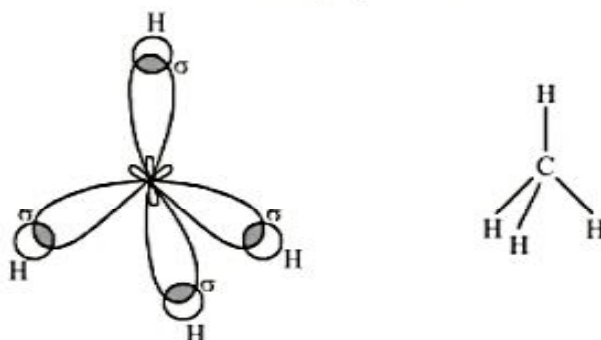
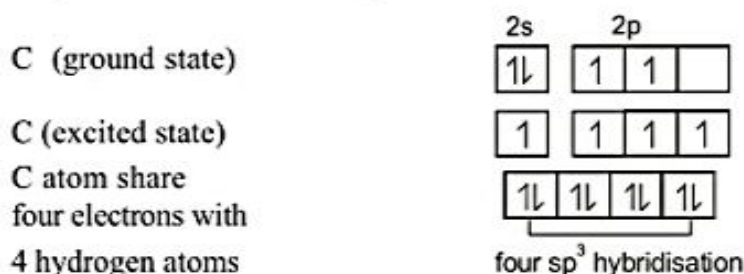
 The shape of SnX<sub>2</sub> molecule is bent.

**Examples on sp<sup>2</sup> hybridisation**

Example	$\sigma$ bond	Lone pair electron	Hybridisation	Bond angle	Shape
BF <sub>3</sub>	3	-	sp <sup>2</sup>	120°	Trigonal planar
$\text{CH}_3^+$	3	-	sp <sup>2</sup>	120°	Trigonal planar
CH <sub>2</sub> =CH <sub>2</sub>	3, 3	-	sp <sup>2</sup>	120°	Trigonal planar
Graphite	3	-	sp <sup>2</sup>	120°	Trigonal planar
NO <sub>3</sub> <sup>-</sup>	3	-	sp <sup>2</sup>	120°	Trigonal planar
HNO <sub>2</sub>	2	1	sp <sup>2</sup>	< 120°	Angular (V-shaped)
SO <sub>2</sub>	2	1	sp <sup>2</sup>	< 120°	Angular (V-shaped)
SO <sub>3</sub>	3	-	sp <sup>2</sup>	120°	Trigonal planar
HCO <sub>3</sub> <sup>-</sup>	3	-	sp <sup>2</sup>	120°	Trigonal planar
SnCl <sub>2</sub>	2	1	sp <sup>2</sup>	< 120°	Angular (V-shaped)
SnI <sub>2</sub>	2	1	sp <sup>2</sup>	< 120°	Angular (V-shaped)
AlCl <sub>3</sub>	3	-	sp <sup>2</sup>	120°	Trigonal planar

**sp<sup>3</sup> Hybridisation :**

- (i) In this hybridisation one s orbital & three p orbitals of an atom of a molecule or ion, are mixed to give four new hybrid orbitals called as sp<sup>3</sup> hybrid orbitals.
- (ii) The angle between these four hybrid orbitals will be 109°28'

Molecular tetrahedral orbital of CH<sub>4</sub>

- (iii) The shape obtained from these hybrid orbitals would be tetrahedron.

Three following examples represent this condition.

**(a) Four sigma bonds with zero lone pair electron :**

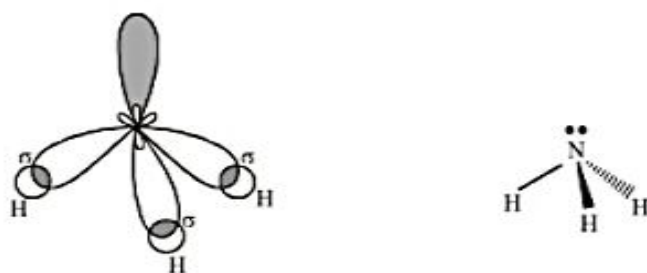
The following examples represent this condition.

CH<sub>4</sub>, CF<sub>4</sub>, CCl<sub>4</sub>, CBr<sub>4</sub>, NH<sub>4</sub><sup>+</sup>, BF<sub>4</sub><sup>-</sup>, BeF<sub>4</sub><sup>-2</sup>, etc.

In above compounds, bond angle is 109°28' & tetrahedron shape.

**(b) Three sigma bonds & one lone pair of electron :**

- (i) This condition is shown by following compounds & ions.

Molecular pyramidal orbital of NH<sub>3</sub>      Molecular pyramidal orbital of NH<sub>3</sub>

NH<sub>3</sub>, NF<sub>3</sub>, PF<sub>3</sub>, NCl<sub>3</sub>, PCl<sub>3</sub>, H<sub>3</sub>O<sup>+</sup>, ClO<sub>3</sub><sup>-</sup> etc.

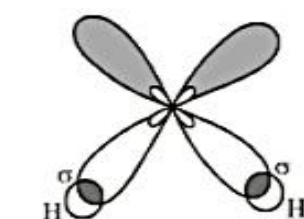
- (ii) sp<sup>3</sup> hybridisation, pyramidal shape & bond angle will be less than 109° 28' due to the presence of the lone pair electron on nitrogen repels bond pair electron more therefore bond angle is reduced from 109°28' to 107°. The repulsion between lone pair – bond pair > bond pair – bond pair.

**(c) Two sigma bonds & two lone pair electrons :**

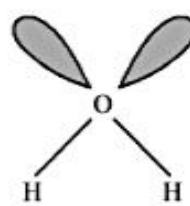
- (i) This condition is shown by following compounds and ions.

H<sub>2</sub>O, OCl<sub>2</sub>, OBr<sub>2</sub>, OF<sub>2</sub>, etc.

(ii) In all above examples, the central atom showing  $sp^3$  hybridisation, angular shape and bond angle will be either less than  $109^\circ 28'$  or more than  $109^\circ 28'$ .



Molecular angular orbital of  $H_2O$



Structure of  $H_2O$   
(Angular)

In  $H_2O$  the hybridisation on O atom is  $sp^3$ , but due to presence of two lone pair electrons they repel each other and then repel their adjacent bond pair electron. These repulsion will be in following order.

$$l.p. - l.p. > l.p. - b.p. > b.p. - b.p.$$

$l.p.$  = lone pair electron

$b.p.$  = bond pair electron

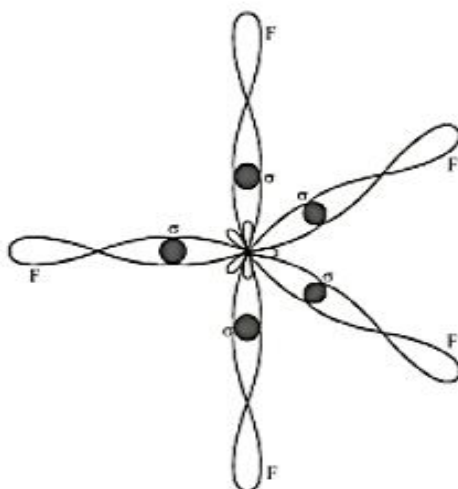
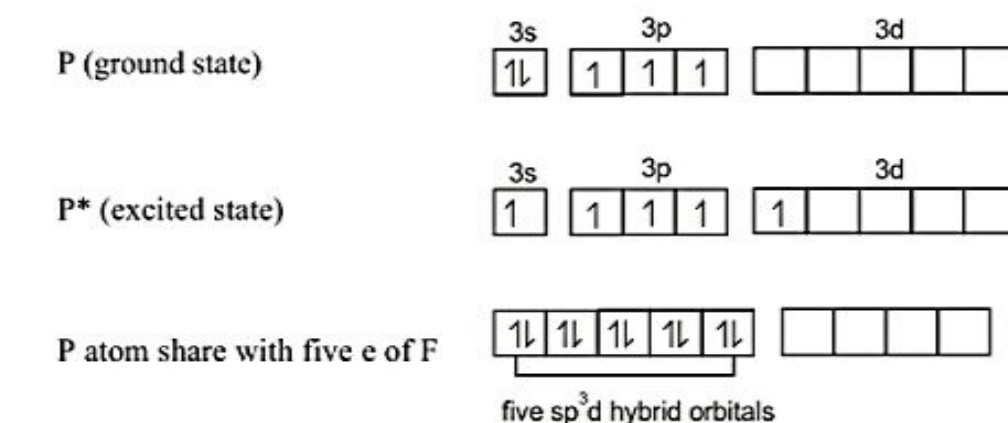
### Examples on $sp^3$ Hybridisation

Example	$\sigma$ bond	lone pair electron	Hybridisation	Shape
$CH_4$	4	-	$sp^3$	Tetrahedron
$PCl_4^+$	4	-	$sp^3$	Tetrahedron
$NH_4^+$	4	-	$sp^3$	Tetrahedron
$BF_4^-$	4	-	$sp^3$	Tetrahedron
$B_2F_4^{-2}$	4	-	$sp^3$	Tetrahedron
$MgF_4^{-2}$	4	-	$sp^3$	Tetrahedron
$NF_3$	3	1	$sp^3$	Pyramidal
$N(CH_3)_3$	3	1	$sp^3$	Pyramidal
$CH_3^-$	3	1	$sp^3$	Pyramidal
$H_3O^+$	3	1	$sp^3$	Pyramidal
$XeO_3$	3	1	$sp^3$	Pyramidal
$NH_2^-$	2	2	$sp^3$	Angular (V-shaped)
$Cl_2O$	2	2	$sp^3$	Angular (V-shaped)
$SCl_2$	2	2	$sp^3$	Angular (V-shaped)
Diamond	4	-	$sp^3$	Tetrahedron
$SiO_2$	4	-	$sp^3$	Tetrahedron
$SiC$	4	-	$sp^3$	Tetrahedron

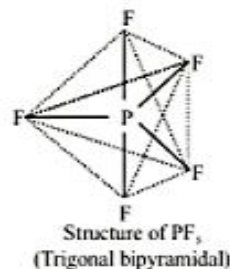
**sp<sup>3</sup>d Hybridisation :**

- (i) In this hybridisation one s orbital, three p-orbital and one d orbital are mixed to give five new hybrid orbitals called as sp<sup>3</sup>d hybrid orbitals.
- (ii) Out of these five orbitals, three hybrid orbitals are at 120° angle and two hybrid orbitals are perpendicular to the plane of three hybrid orbitals that is trigonal planar, the shape of molecule becomes is trigonal bipyramidal.

For example, PF<sub>5</sub> showing sp<sup>3</sup>d hybridisation



Molecular trigonal bipyramidal orbital of PF<sub>5</sub>



- (iii) In this hybridisation d<sub>z<sup>2</sup></sub> orbital is hybridised with s and p orbitals.

In this way five sp<sup>3</sup>d hybrid orbitals form five sigma bond with five F atoms and give a molecule of PF<sub>5</sub>, shape of this molecule is trigonal bipyramidal.

Axial two P–Cl bonds are longer than equatorial three P–Cl bond due to repulsion between 3 equatorial bond pair of electron and 2 axial bond pair of electron.

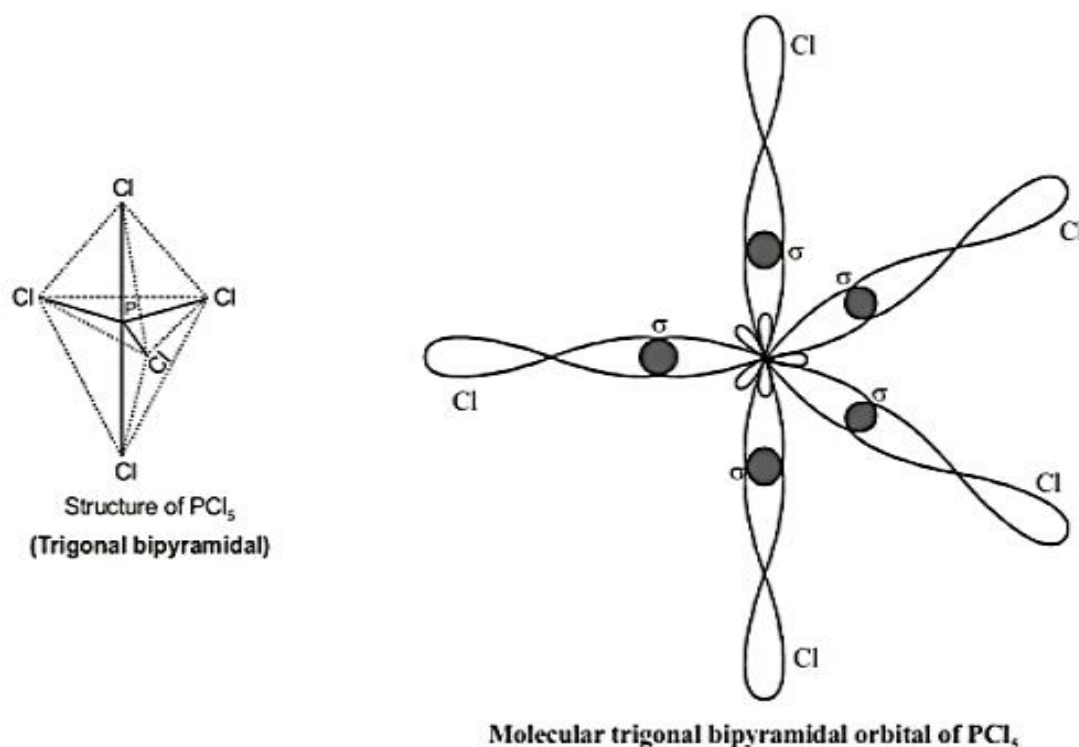
In above hybridisation there are four conditions

**(a) Five sigma bonds and zero lone pair electron :**

The following examples represent this conditions.

PF<sub>5</sub>, PCl<sub>5</sub>, PBr<sub>5</sub>, PI<sub>5</sub>, AsF<sub>5</sub>, AsCl<sub>5</sub>, SbCl<sub>5</sub>, SbF<sub>5</sub> etc.





The shape of all above molecules is trigonal bipyramidal.

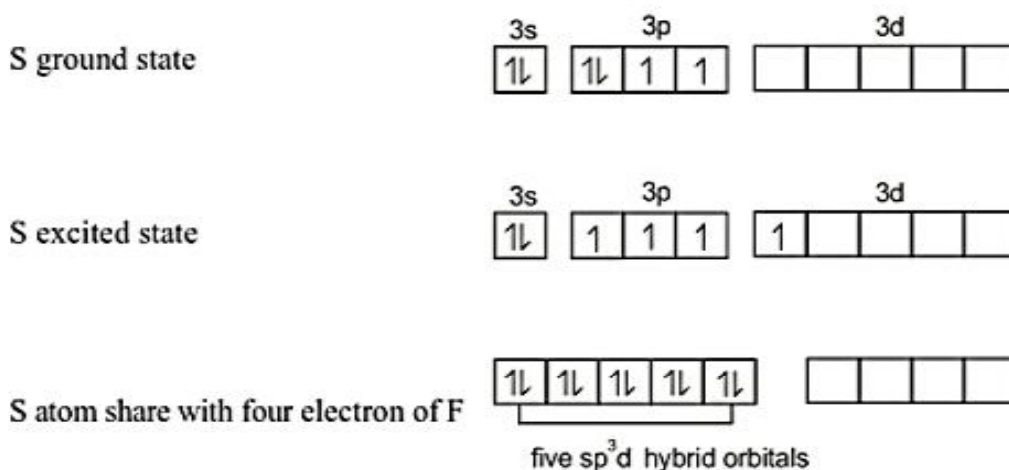
**(b) Four sigma bonds and one lone pair of electron :**

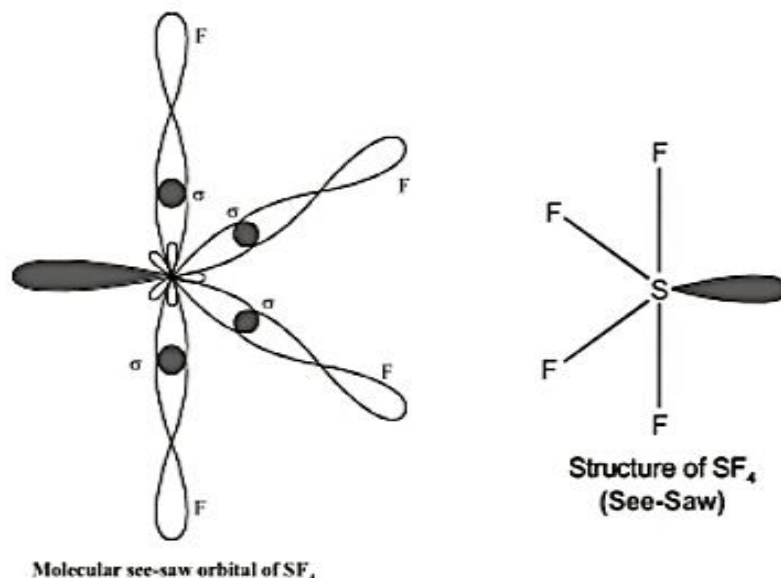
The following examples represent this condition.

$\text{SF}_4$ ,  $\text{SeF}_4$ ,  $\text{TeF}_4$ ,  $\text{PoF}_4$ ,  $\text{PF}_4^-$ ,  $\text{SbF}_4^-$ ,  $\text{SCl}_4$ ,  $\text{SeCl}_4$ ,  $\text{TeCl}_4$  etc.

The shape of all above examples will be irregular tetrahedron/see saw.

Examples  $\text{SF}_4$



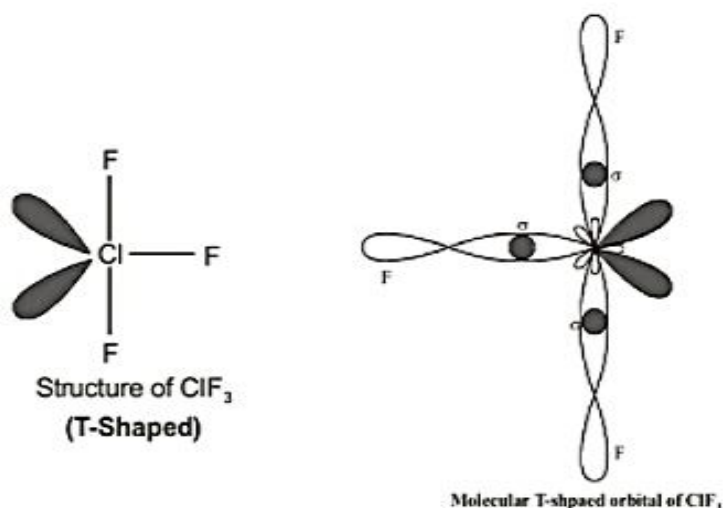


(c) **Three sigma bonds & two lone pair of electrons :**

The following examples represent this condition.

ClF<sub>3</sub>, BrF<sub>3</sub>, IF<sub>3</sub>, BrCl<sub>3</sub>, ICl<sub>3</sub> etc.

The shape of all above compounds is 'T' shape.



(d) **Two sigma bonds & three lone pair of electrons :**

The following examples represent this condition.

ICl<sub>2</sub><sup>-</sup>, IBr<sub>2</sub><sup>-</sup>, ClF<sub>2</sub><sup>-</sup>, IF<sub>2</sub><sup>-</sup>, BrF<sub>2</sub><sup>-</sup>, XeF<sub>2</sub>, I<sub>3</sub><sup>-</sup>, Br<sub>3</sub><sup>-</sup>

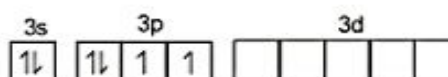
The geometry of above examples will be linear

**sp<sup>3</sup>d<sup>2</sup> Hybridisation :**

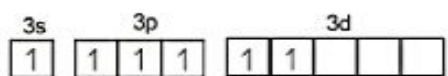
- (i) In this hybridisation, one s-orbital, three p-orbitals & two d-orbitals are mixed to give six new hybrid orbitals known as sp<sup>3</sup>d<sup>2</sup> hybrid orbitals.
  - (ii) The shape of molecule obtained from above six hybrid orbitals will be symmetrical octahedral.
  - (iii) The angle between all hybrid orbitals will be 90°.
- Example : SF<sub>6</sub>, AlF<sub>6</sub><sup>-3</sup>, PF<sub>6</sub><sup>-</sup>, ICl<sub>5</sub>, XeF<sub>4</sub>, XeOF<sub>4</sub>, ICl<sub>4</sub><sup>-</sup>,
- (iv) Two 'd' orbital participates in the hybridisation are d<sub>x<sup>2</sup>-y<sup>2</sup></sub> and d<sub>z<sup>2</sup></sub>.

**SF<sub>6</sub> :**

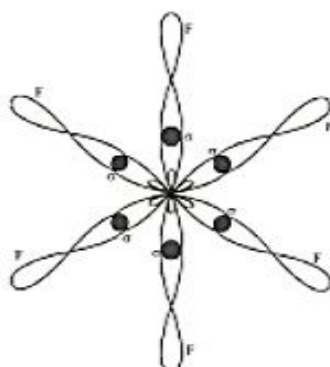
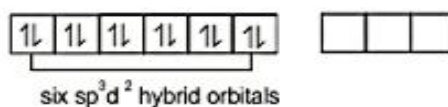
S (ground state)



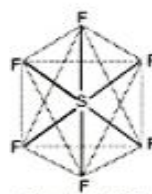
S (excited state)



S (after hybridisation)



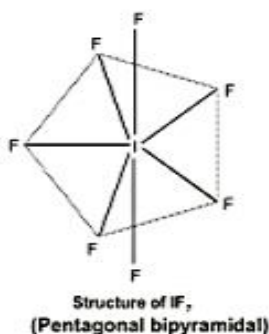
Molecular orbital of SF<sub>6</sub>



Structure of SF<sub>6</sub>  
(Octahedral)

### **sp<sup>3</sup>d<sup>3</sup> Hybridisation :**

- In this hybridisation, one s-orbital, three p-orbitals & three d-orbitals are mixed to give seven new hybrid orbitals known as  $sp^3d^3$  hybrid orbitals.
- In this hybridisation d-orbitals used are  $d_{xy}$ ,  $d_{x^2-y^2}$  &  $d_{z^2}$  orbitals.
- These seven  $sp^3d^3$  orbitals are configured in pentagonal bipyramidal shape.
- Five bond angles are of  $72^\circ$  & two hybrid orbitals are perpendicular to the plane of five hybrid orbitals that is pentagonal planar, the shape of molecule becomes pentagonal bipyramidal.
- The following examples showing  $sp^3d^3$  hybridisation : IF<sub>7</sub> & XeF<sub>6</sub>.



Structure of IF<sub>7</sub>  
(Pentagonal bipyramidal)

### **Illustration**

- Which of the following statement is not correct?
  - Hybridization is the mixing of atomic orbitals
  - $sp^2$  – hybrid orbitals are formed from two p - atomic orbitals and one s- atomic orbitals
  - $dsp^2$  – hybrid orbitals are at  $90^\circ$  to one another
  - $d^2sp^3$  – hybrid orbitals are directed towards the corners of a regular octahedron

**Ans.** (A)

**Sol.** Hybridization is the mixing of atomic orbitals having comparable energy.

2. The correct order of increasing s-character (in percentage) in the hybrid orbitals of following molecules/ions is:

(I)  $\text{CO}_3^{2-}$  (II)  $\text{XeF}_4$  (III)  $\text{I}_3^-$  (IV)  $\text{NCl}_3$  (V)  $\text{BeCl}_2$   
 (A) II<III<IV<I<V (B) II<IV<III<V<I (C) III<II<I<V<IV (D) II<IV<III<I<V

Ans. (A)

Sol.  $\text{CO}_3^{2-} \rightarrow \text{sp}^2$  % s character = 33.3%  
 $\text{XeF}_4 \rightarrow \text{sp}^3\text{d}^2$  16.6%  
 $\text{I}_3^- \rightarrow \text{sp}^3\text{d}$  20%  
 $\text{NCl}_3 \rightarrow \text{sp}^3 = 25\%$   
 $\text{BeCl}_2 \rightarrow \text{sp}$  50%

### Exercise

1. Which of the following statement is incorrect?  
 (A)  $\text{NH}_2^+$  shows  $\text{sp}^2$  – hybridisation whereas  $\text{NH}_2^-$  shows  $\text{sp}^3$  – hybridisation  
 (B)  $\text{Al}(\text{OH})_4^-$  has a regular tetrahedral geometry  
 (C)  $\text{sp}^2$  – hybridized orbitals have equal s- and p- character  
 (D) Usually hybridized orbitals form  $\sigma$  - bonds

Ans. (C)

2. Which is correct statement?  
 As the s-character of a hybrid orbital decreases  
 (I) The bond angle decreases (II) The bond strength increases  
 (III) The bond length increases (IV) Size of orbital increases  
 (A) (I), (III) and (IV) (B) (II), (III) and (IV) (C) (I) and (II) (D) All are correct

Ans. (A)

## HYBRIDISATION IN SOLID STATE / AQUEOUS STATE OF MOLECULES

Hybridization of covalent species which exist in ionic form in solid state.

Gaseous State	Hybridization	Solid State	Hybridization (Cation)	Hybridization (Anion)
$\text{PCl}_5$	$\text{sp}^3\text{d}$	$[\text{PCl}_4]^+ + [\text{PCl}_6]^-$	$\text{sp}^3$	$\text{sp}^3\text{d}^2$
$\text{PBr}_5$	$\text{sp}^3$	$[\text{PBr}_4]^+ + \text{Br}^-$	$\text{sp}^3$	
$\text{XeF}_6$	$\text{sp}^3\text{d}^3$	$[\text{XeF}_5]^+ + \text{F}^-$	$\text{sp}^3\text{d}^2$	
$\text{N}_2\text{O}_5$	$\text{sp}^2$	$[\text{NO}_2]^+ + [\text{NO}_3]^-$	$\text{sp}$	$\text{sp}^2$
$\text{N}_2\text{O}_4$		$[\text{NO}]^+ + [\text{NO}_3]^-$		$\text{sp}^2$
$\text{N}_2\text{O}_3$	$\text{sp}^2$	$[\text{NO}]^+ + [\text{NO}_2]^-$		$\text{sp}^2$
$\text{BrF}_3$	$\text{sp}^3\text{d}$	$[\text{BrF}_2]^+ + [\text{BrF}_4]^-$	$\text{sp}^3$	$\text{sp}^3\text{d}^2$
$\text{IF}_5$	$\text{sp}^3\text{d}^2$	$[\text{IF}_4]^+ + [\text{IF}_6]^-$	$\text{sp}^3\text{d}$	$\text{sp}^3\text{d}^3$
$\text{ICl}$		$[\text{I}_2\text{Cl}]^+ + [\text{ICl}_2]^-$	$\text{sp}^3$	$\text{sp}^3\text{d}$
$\text{Cl}_2\text{O}_6$	$\text{sp}^3$	$[\text{ClO}_2]^+ + [\text{ClO}_4]^-$	$\text{sp}^2$	$\text{sp}^3$
$\text{I}_4\text{O}_9$		$\text{I}^{3+} + [\text{IO}_3]^-_3$		$\text{sp}^3$
$\text{I}_2\text{Cl}_{6(l)}$		$[\text{ICl}_2]^+ + [\text{ICl}_4]^-$	$\text{sp}^3$	$\text{sp}^3\text{d}^2$
$\text{I}_2$		$[\text{I}_3]^+ + [\text{I}_3]^-$	$\text{sp}^3$	$\text{sp}^3\text{d}$
$\text{ICN}$	$\text{sp}$ (C)	$[\text{I}_2\text{CN}]^+ + [\text{I}(\text{CN})_2]^-$	$\text{sp}^3$ (I)	$\text{sp}^3\text{d}$ (I)





In  $AB_x$  type molecules, if central atoms are same and the Electronegativity of side atoms increases then bond angle decreases.



Electronegativity of Fluorine is greater than chlorine

$PF_3 < PCl_3 < PBr_3 < PI_3$  (Electronegativity of side atom decrease)

$OF_2 < Cl_2O < Br_2O$

$SF_2 < SCl_2 < SBr_2$

Bond angle depends on size of side atom, On increasing size of side atom bond angle increases.

$Cl_2O > H_2O$



### Illustration

1. Arrange the following in order of decreasing  $N-O$  bond length:  $NO_2^+$ ,  $NO_2^-$ ,  $NO_3^-$   
 (A)  $NO_3^- > NO_2^+ > NO_2^-$  (B)  $NO_3^- > NO_2^- > NO_2^+$  (C)  $NO_2^+ > NO_3^- > NO_2^-$  (D)  $NO_2^- > NO_3^- > NO_2^+$   
 Ans. (B)

Sol. Bond order  $\propto \frac{1}{\text{Bond length}}$

	$NO_2^+$	$NO_2^-$	$NO_3^-$
Bond order	2	1.5	1.33

### Exercise

1. Comment on the  $\angle CNC$  and  $\angle HNN$  in  $CH_3NCS$  and  $HN_3$  respectively.  
 (A) less than  $120^\circ$  and less than  $120^\circ$  (B) Greater than  $120^\circ$  and less than  $120^\circ$   
 (C) less than  $120^\circ$  and greater than  $120^\circ$  (D) Greater than  $120^\circ$  and greater than  $120^\circ$   
 Ans. (B)
2. The correct order of decreasing  $X-O-X$  bond angle is ( $X = H, F$  or  $Cl$ ):  
 (A)  $H_2O > Cl_2O > F_2O$  (B)  $Cl_2O > H_2O > F_2O$  (C)  $F_2O > Cl_2O > H_2O$  (D)  $F_2O > H_2O > Cl_2O$   
 Ans. (B)

### DRAGO'S RULE

According to Drago, when central atom of the compound is of 3rd period or below this of periodic table then lone pair is present in stereo chemically inactive s-orbital and bonding will take place through pure p-orbitals. But electronegativity of the surrounding atom must be less than or equal to 2.5. Then there is no hybridization and bond angle is nearly  $90^\circ$ .

$NH_3$  ( $107.8^\circ$ ),  $PH_3$  ( $93.6^\circ$ ),  $AsH_3$  ( $91.8^\circ$ ),  $SbH_3$  ( $91.3^\circ$ )

### Illustration

1. Among the following, the correct statement is :
- (A) Between  $\text{NH}_3$  and  $\text{PH}_3$ ,  $\text{NH}_3$  is a better electron donor because the lone pair of electrons occupies spherical 's' orbital and is less directional
- (B) Between  $\text{NH}_3$  and  $\text{PH}_3$ ,  $\text{PH}_3$  is a better electron donor because the lone pair of electrons occupies  $\text{sp}^3$  orbital and is more directional
- (C) Between  $\text{NH}_3$  and  $\text{PH}_3$ ,  $\text{NH}_3$  is a better electron donor because the lone pair of electrons occupies  $\text{sp}^3$  orbital and is more directional
- (D) Between  $\text{NH}_3$  and  $\text{PH}_3$ ,  $\text{PH}_3$  is a better electron donor because the lone pair of electrons occupies spherical 's' orbital and is less directional

Ans. (C)

Sol.  $\text{NH}_3 \rightarrow \text{sp}^3$  hybridisation (directional property),

$\text{PH}_3 \rightarrow$  No hybridisation

So the  $\text{NH}_3$  is a better lewis base than  $\text{PH}_3$

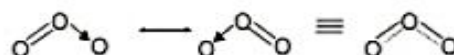
### Exercise

1. The bond angle in  $\text{PH}_3$  is :
- (A) Much lesser than  $\text{NH}_3$  (B) Equal to that in  $\text{NH}_3$
- (C) Much greater than in  $\text{NH}_3$  (D) Slightly more than in  $\text{NH}_3$

Ans. (A)

## RESONANCE

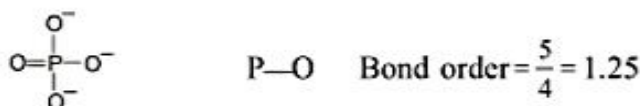
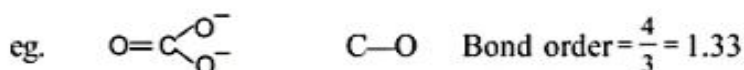
- (i) The concept of resonance was introduced by Heisenberg (1920), and later developed by Pauling and Ingold, to explain the properties of certain molecules,
- (ii) It has been found that the observed properties of certain compounds cannot be satisfactorily explained by writing a single Lewis structure. The molecule is then supposed to have many structures, each of which can explain most of the properties of the molecule but none can explain all the properties of the molecules. The actual structure is in between of all these contributing structures and is called resonance hybrid and the different individual structures are called resonating structures or canonical forms. This phenomenon is called resonance.
- (iii) Let us discuss resonance in ozone, according to its resonating structure it should have one single bond ( $\text{O}-\text{O} = 1.48\text{\AA}$ ) but experiments show that both the bonds are same which can be proved by its resonance hybrid as shown below.



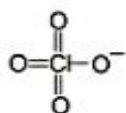
Resonance hybrid

To calculate bond order in the polyatomic molecule or ion use following formula :

$$\text{Bond order} = \frac{\text{Total number of bonds in a molecule}}{\text{Resonating Structures}}$$







$$\text{Cl}-\text{O} \quad \text{Bond order} = \frac{7}{4} = 1.75$$

**Illustration**

1. (C—Cl) bond in  $\text{CH}_2=\text{CH}-\text{Cl}$  (vinyl chloride) is stabilised in the same way as in:  
 (A) benzyl chloride (B) ethyl chloride (C) chlorobenzene (D) allyl chloride  
**Ans.** (C)  
**Sol.** Both the molecule shows resonance

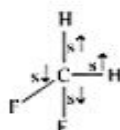
**Exercise**

1. Which of the following option is **incorrect**?  
 (I) All C—O bonds in  $\text{CO}_3^{2-}$  are equal but not in  $\text{H}_2\text{CO}_3$ .  
 (II) All C—O bonds in  $\text{HCO}_2^-$  are equal but not in  $\text{HCO}_2\text{H}$   
 (III) C—O bond length in  $\text{HCO}_2^-$  is longer than C—O bond length in  $\text{CO}_3^{2-}$ .  
 (IV) C—O bond length in  $\text{HCO}_2^-$  and C—O bond length in  $\text{CO}_3^{2-}$  are equal.  
 (A) III & IV (B) II & III (C) II & IV (D) I & IV  
**Ans.** (A)
2. Resonance does not occur due to the  
 (A) delocalization of a lone pair of electrons (B) delocalization of sigma electrons  
 (C) delocalization of pi electrons (D) None of these  
**Ans.** (B)

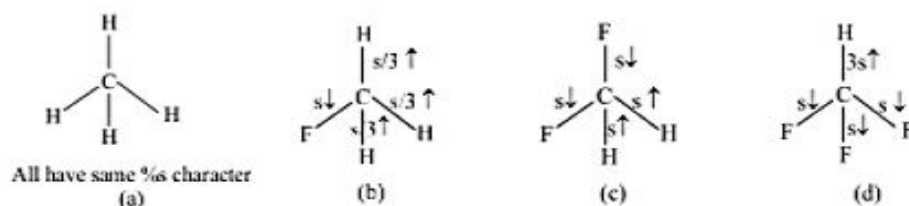
**BENT RULE**

When all hybrid orbitals equivalent. Ex.  $\text{sp}^3$ ,  $\text{sp}^2$

- (1) If the more EN atom present in hybrid orbital, %s character decreases.



to compensate decrement of %s character these %s character increases on that orbital which have less EN atom bonded.

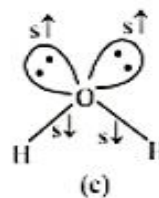
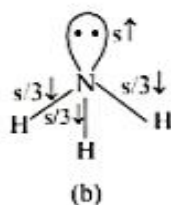
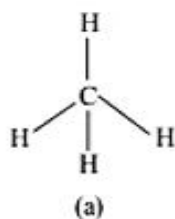
**Example-1**

C—H bond length  $a > b > c > d$   
 HCF bond angle  $b < c < d$



- (2) If the L.P is present in hybrid orbital, %s character increases

### Example-2

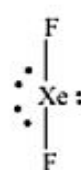
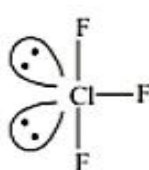
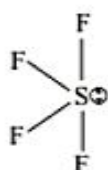
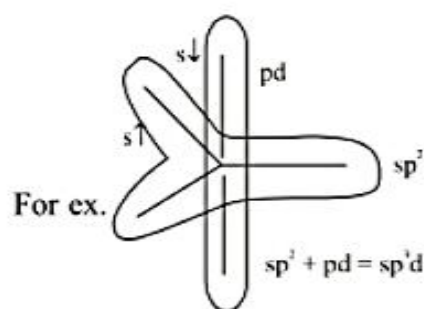


H × H bond angle  $a > b > c$  (X = Central atom)

If hybrid orbital are not equivalent

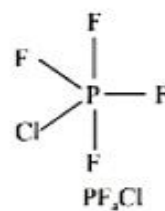
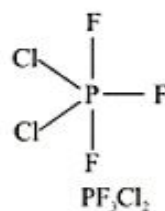
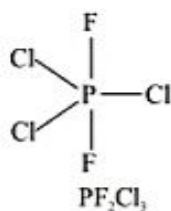
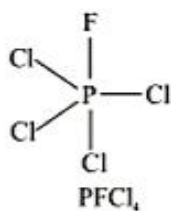
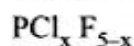
L.p. acquire place where %s character are higher

### Example-3



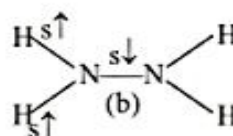
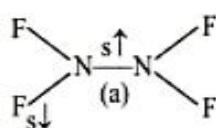
More EN atom acquire place where %s character are less

### Example-4

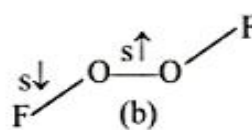
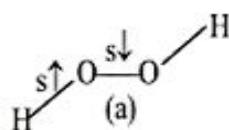


## Bond length comparison

## Example-5

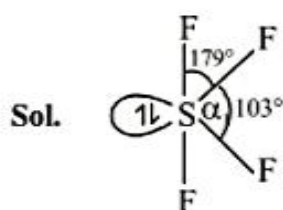
N-N bond length  $a < b$ 

## Example-6

O-O bond length  $a > b$ 

## Illustration

1. Comment on the effect of lone pair on axial and equatorial bond angles of  $\text{SF}_4$ .



As expected axial bond should distort more than equatorial but actually due to lone pair has tendency to goes with more % character available bond angle decreases more than axial one.  
Equatorial F—S—F angle will be  $120^\circ$  but it is  $103^\circ$ ]

2. Axial B.A. in  $(\text{SF}_4) > \text{CH}_2 = \text{SF}_4$ . Why?

Sol.

Axial	$179^\circ$	$178.5^\circ$	$170^\circ$
Equatorial	$103^\circ$	$110^\circ$	$97^\circ$

## Exercise

1. The strongest P—O bond is found in the molecule

(A)  $\text{F}_3\text{PO}$ (B)  $\text{Cl}_3\text{PO}$ (C)  $\text{Br}_3\text{PO}$ (D)  $(\text{CH}_3)_3\text{PO}$ 

Ans. (A)

## BACK BONDING

The one sided sharing of electron pair present in the outer orbital of an atom with the empty orbital present in the adjacent atom. It leads to the formation of a  $\pi$  coordinate bond.

### Condition for back bonding

The donor atom must have localized donatable electron pair. In general these are later half, second period P - block elements (F, O, N and C). The acceptor atom must have low energy empty orbital which generally are np or nd orbitals. Small and similar sized orbitals favour overlap.

### Effects of back bonding

1. It always leads to an increase in bond order between the participating atoms.
2. It always leads to an increase in bond strength between participating atoms.
3. It always leads to a decrease in bond length between participating atoms.
4. It decreases the lewis acid character of the acceptor atom as the low energy empty orbital is now filled and not available for accepting the electron from a lewis base. This is evident in case of boron halides. Boron and fluorine are the members of the same period and hence have orbitals having similar size and energy. This allows fluorine to effectively donate the electrons from its filled p orbitals to the empty unhybridized orbital of boron. This makes  $\text{BF}_3$  much weaker lewis acid than  $\text{BCl}_3$  which in turn is a weaker lewis acid than  $\text{BBr}_3$ .

Structural formula of boron trifluoride,  $\text{BF}_3$ , showing  $\pi$  bonding involving filled fluorine 2p orbitals (formally lone pairs) overlapping with the empty 2p orbital on boron and donating electron density to relieve boron's electron deficiency.

This can easily be explained by the increase in size of the halogen atom, its orbitals and decreased capacity to donate electron towards back-bonding as we move down the group. The Lewis acidity scale of boron trihalides  $\text{BX}_3$  ( $\text{X}=\text{F}, \text{Cl}, \text{Br}, \text{I}$ ) and character of the boron-halogen bonds have been studied by means of DV-Xm approach. Present results show that the acid strength of boron trihalides increases in the order  $\text{BF}_3 < \text{BCl}_3 < \text{BBr}_3 < \text{BI}_3$ , in excellent agreement with experiments.

5. It decreases the lewis base character of the donor atom as now its electrons are not free for donation. This is evident in comparison of the lewis base character of  $\text{N}(\text{SiH}_3)_3$  and  $\text{N}(\text{CH}_3)_3$ . In trisilyl amine the lone pair of nitrogen is involved in back bonding with empty 3d orbital of silicon. Hence it is not available for donation. This makes it much weaker base in comparison to trimethyl amine. (Another comparison could be pyrrol and pyridine, aniline and methyl amine)
6. It either increases the bond angle or the bond angle remains the same but never decreases. The bond angle increases when the donation is from the peripheral atom towards the central atom as in case of  $\text{PF}_3$ . In it the electron pair from the filled p orbital of fluorine moves into the empty 3d orbital of phosphorus. This increases the electron density in the phosphorus fluorine bond and



increases the bond pair - bond pair repulsion. This makes the F-P-F bond angle in  $\text{PF}_3$  ( $98^\circ$ ) greater than H-P-H bond in  $\text{PH}_3$  ( $94^\circ$ ). The bond angle increases even when the donation is from the central atom towards the peripheral atom as in the case of trisilyl amine,  $(\text{SiH}_3)_3\text{N}$ . Nitrogen donates the lone pair in its p orbital to the empty d orbital of Si. This decreases the electron density on nitrogen and with that the lone pair - bond pair repulsion also decreases. The hybridization of nitrogen changes from  $\text{sp}^3$  to  $\text{sp}^2$ . And so the bond angle becomes almost  $120^\circ$ . Same is the case with  $(\text{SiH}_3)_2\text{O}$  ( $144^\circ$ ) compared to  $(\text{CH}_3)_2\text{O}$  ( $110^\circ$ ).  $\text{CH}_3\text{-NCS}$  is bent whereas  $\text{SiH}_3\text{-NCS}$  is linear.

In some cases like  $\text{BF}_3$ , there is no change in the bond angle due to the back bonding.

7. Complex formation tendency of certain ligands which have back bonding in them is affected.  $(\text{CH}_3)_2\text{O}$  readily forms complex with  $\text{BF}_3$  but  $(\text{SiH}_3)_2\text{O}$  does not as here the lone pair of O is utilized in back bonding with Si.
8.  $\text{HCCl}_3$  is more acidic than  $\text{HCF}_3$ . Although F is more electronegative than Cl and hence should make the negative charge more stable by dispersing it through inductive effect. But the observation suggests that the conjugate of  $\text{CHCl}_3$ ,  $-\text{CCl}_3$  is more stable than  $-\text{CF}_3$ . This can be explained by considering the transfer of electron pair from carbon to empty d orbital of Cl leading to a better dispersal of negative charge.
9. Carbenes: Dichloro and difluoro carbenes ( $\text{CCl}_2$  and  $\text{CF}_2$ ) due to back bonding from the side of halogen prefer to exist in the singlet state. Whereas for  $\text{CH}_2$  the triplet is the more stable state.

### Illustration

1. From the given set of molecules select the group in which 1st molecule has less acidic character in comparison of 2nd molecule  
 (A)  $\text{CHCl}_3$ ,  $\text{CHF}_3$  (B)  $\text{BF}_3$ ,  $\text{BCl}_3$   
 (C)  $(\text{SiH}_3)_2\text{O}$ ,  $\text{O}(\text{CH}_3)_2$  (D)  $(\text{CH}_3)_3\text{SiOH}$ ,  $(\text{CH}_3)_3\text{COH}$

Ans. (B)

Sol. Due to the presence of effective  $\text{p}\pi - \text{p}\pi$  backbonding in  $\text{BF}_3$ ; it is less acidic than  $\text{BCl}_3$

### Exercise

1. Boron forms  $\text{BX}_3$  type of halides. The correct decreasing order of Lewis-acid strength of these halides is  
 (A)  $\text{BF}_3 > \text{BCl}_3 > \text{BBr}_3 > \text{BI}_3$  (B)  $\text{BI}_3 > \text{BBr}_3 > \text{BCl}_3 > \text{BF}_3$   
 (C)  $\text{BF}_3 > \text{BI}_3 > \text{BCl}_3 > \text{BBr}_3$  (D)  $\text{BF}_3 > \text{BCl}_3 > \text{BI}_3 > \text{BBr}_3$

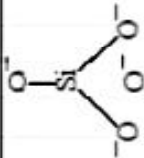
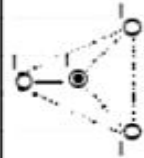



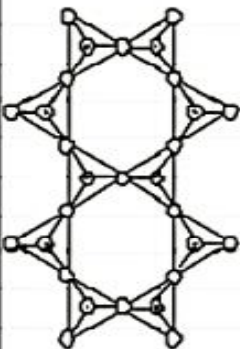
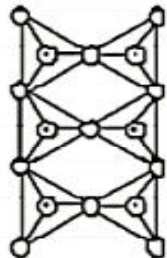
Ans. (B)

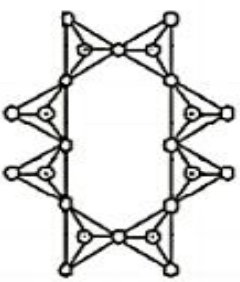
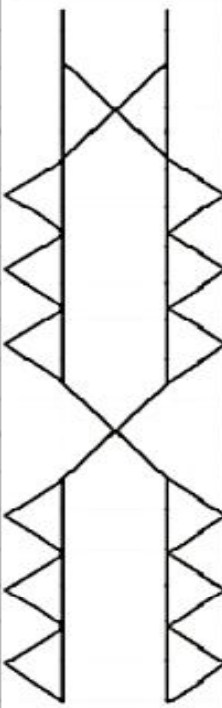
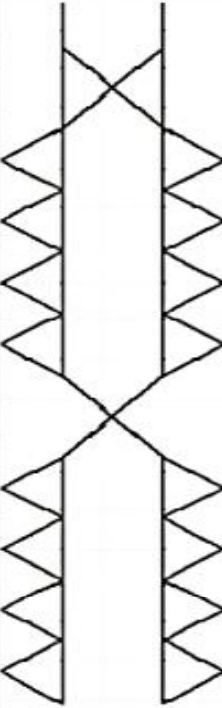

## SILICATES

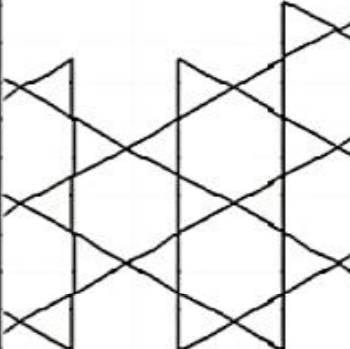
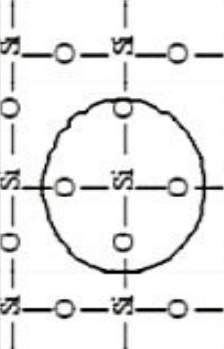
The way in which the  $(\text{SiO}_4)^{4-}$  tetrahedral units are linked together provides a convenient classification of the many silicate minerals.

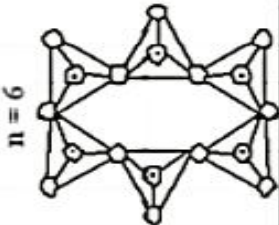
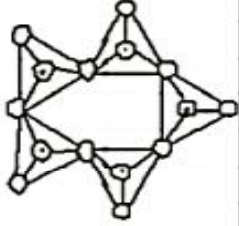
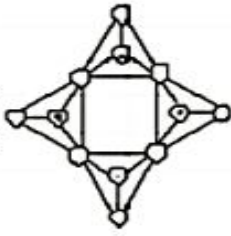
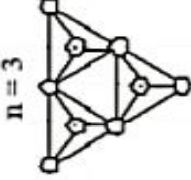


## Classification of Silicates

Types of Silicates	No. of 'O' Shared Per molecule	General Formula	General Formula if Restricted	Structure
Ortho silicate [Neso silicate]	Zero	$[\text{SiO}_4]^{4-}$	$[\text{SiO}_4]^{4-}$	 
Pyro silicate [Soro silicate]	One	$[\text{Si}_2\text{O}_7]^{6-}$	$[\text{Si}_2\text{O}_7]^{6-}$	
Single chain Silicate Pyroxene	Two 'O'	$[\text{SiO}_3]_{2n}^{2n-}$	$[(\text{SiO}_3)_n]^{2n-} + \text{O}^{2-}$	 
Double chain Amphibole	$2 > \text{'O'} \leq 3$	$\text{SiO}_{4-1/2 \times n}^{4+n}$ $n = \text{no. of 'O' shared per tetrahedron}$  if $n = 5/2$ , $[\text{Si}_4\text{O}_{11}]_n^{6n-}$	$[\text{SiO}_{4-1/2 \times n}^{4+n} + 2\text{O}^{2-}]$  $[(\text{Si}_4\text{O}_{11})_n]^{6n-} + 2\text{O}^{2-}$	 

Types of Silicates	No. of 'O' Shared Per molecule	General Formula	General Formula if Restricted	Structure
		if $n = 3$ $[\text{Si}_2\text{O}_5]_n^{2n-}$ -----	$[(\text{Si}_2\text{O}_5)_n]^{2n-} + 2\text{O}^{2-}$	
		if $n = 7/3$ , $[\text{Si}_6\text{O}_{17}]_n^{10n-}$ -----	$[(\text{Si}_6\text{O}_{17})_n]^{6n-} + 2\text{O}^{2-}$	
		$n = 9/4$ $[\text{Si}_8\text{O}_{23}]_n^{14n-}$	$[(\text{Si}_8\text{O}_{23})_n]^{14n-} + 2\text{O}^{2-}$	
		if $n = 11$ $[\text{Si}_{10}\text{O}_{29}]_n^{18n-}$	$[(\text{Si}_{10}\text{O}_{29})_n]^{18n-} + 2\text{O}^{2-}$	

Types of Silicates	No. of 'O' Shared Per molecule	General Formula	General Formula if Restricted	Structure
2-D sheet silicate [Phyllosilicate]	3 'O'	$n^+ [\text{Si}_2\text{O}_5]_n^{2n-}$	$n^+ [[\text{Si}_2\text{O}_5]_n^{2n-} + \text{O}^{2-}]$ where $n = [\text{Si}_2\text{O}_5]^{2-}$ units $n^+ = \text{no. of layers}$	
3-D Sheet silicate	4 'O'	$(\text{SiO}_2)_n$	$(\text{SiO}_2)_n$	

Types of Silicates	No. of 'O' Shared Per molecule	General Formula	General Formula if Restricted	Structure
Ring Silicate Or cyclic silicate	2 'O'	$[\text{SiO}_3]_n^{2n-}$	$[\text{SiO}_3]_n^{2n-}$	<div></div>



### Illustration

1. The following pictures represent various silicate anions. Their formulae are respectively:



- (A)  $\text{SiO}_3^{2-}$        $\text{Si}_3\text{O}_7^{2-}$       (B)  $\text{SiO}_4^{4-}$        $\text{Si}_3\text{O}_{10}^{8-}$   
 (C)  $\text{SiO}_4^{2-}$        $\text{Si}_3\text{O}_9^{2-}$       (D)  $\text{SiO}_3^{4-}$        $\text{Si}_3\text{O}_7^{8-}$

Ans. (B)

Sol. (I) Orthosilicate is  $\text{SiO}_4^{4-}$

(II) Ist & last are chain terminating unit. So the molecular formula is  
 $\text{SiO}_{3.5}^{3-} + \text{SiO}_3^{2-} + \text{SiO}_{3.5}^{3-}$

2.  $\text{Si}_2\text{O}_7^{6-}$  anion is obtained when

- (A) no oxygen of a  $\text{SiO}_4$  tetrahedron is shared with another  $\text{SiO}_4$  tetrahedron.  
 (B) one oxygen of a  $\text{SiO}_4$  tetrahedron is shared with another  $\text{SiO}_4$  tetrahedron.  
 (C) two oxygen of a  $\text{SiO}_4$  tetrahedron are shared with another  $\text{SiO}_4$  tetrahedron.  
 (D) three or all four oxygens of a tetrahedron are shared with other  $\text{SiO}_4$  tetrahedron.

Ans. (B)

Sol. Pyrosilicate  $\rightarrow$  no. of oxygen shared in each tetrahedron is 1.

### Exercise

1.  $\text{Si}_3\text{O}_9^{6-}$  (having three tetrahedral) is represented as:



Ans. (B)

2. The silicate anion in the mineral kinoite is a chain of three  $\text{SiO}_4$  tetrahedra that share corners with adjacent tetrahedra. The mineral also contains  $\text{Ca}^{2+}$  ions,  $\text{Cu}^{2+}$  ions, and water molecules in a 1:1:1 ratio mineral is represented as:

- (A)  $\text{CaCuSi}_3\text{O}_{10} \cdot \text{H}_2\text{O}$  (B)  $\text{CaCuSi}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$  (C)  $\text{Ca}_2\text{Cu}_2\text{Si}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$  (D) none of these

Ans. (C)

### BRIDGE BOND

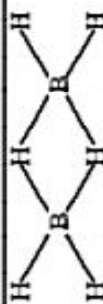
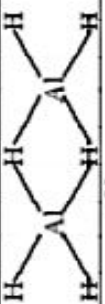


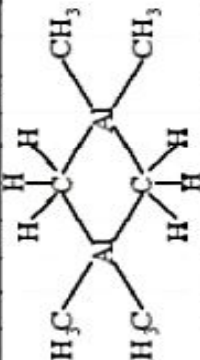
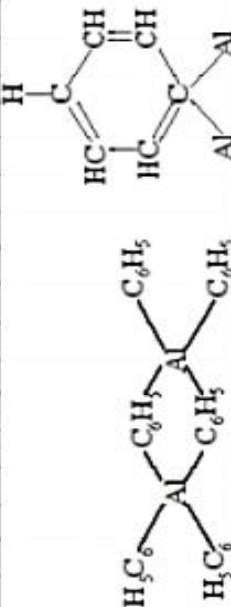
When a species seems to be exceeding its valence in a bid to join two species the bond is termed as the bridge bond.

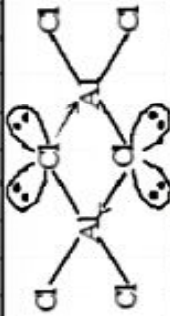
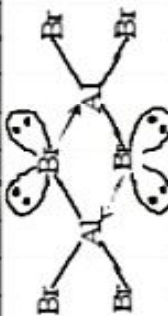
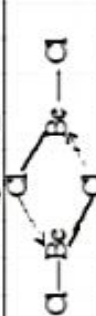

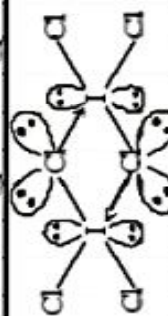

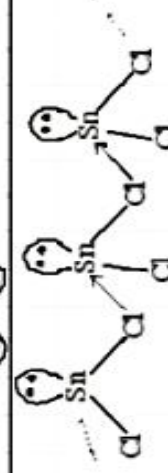
The main reason for the formation of the bridge bond is to complete the octet. This is the main but not the only reason. There could be species which have octet already exceeded and still they try to gain more electrons by the formation of the bridge bond. It seems that the reason is just the availability of low energy empty orbitals.

The first preference of every species is to satisfy the valency within the molecule. That is the back bonding. The bridge bond is formed when a species cannot satisfy the electron deficiency by back bonding.

The bridge bonds are of two types:

1. The electron deficient bridge bond. It is formed by hydrogen, alkyl or boron.
2. Coordinate bridge bonds. These are formed by the species which have an extra donatable electron pair in their valence shell. These are generally formed by halogens.

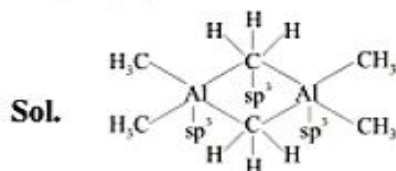
Compound	Bridge	Hybridisation	Planar / Non Planar	Structure
$B_2H_6$	$3c - 2e^-$	$sp^3 - s - sp^3$	Non planar	
$Al_2H_6$	$3c - 2e^-$	$sp^3 - s - sp^3$	Non planar	
$Be_2H_4$	$3c - 2e^-$	$sp^3 - s - sp^3$	Planar	
$(BeH_2)_n$	$3c - 2e^-$	$sp^3 - s - sp^3$	Non Planar	
$Al_2(CH_3)_6$	$3c - 2e^-$	$sp^3 - sp^3 - sp^3$	Non planar	
$Al_2(C_6H_5)_6$	$3c - 2e^-$	$sp^3 - sp^2 - sp^3$	Non planar	

Compound	Bridge	Hybridisation	Planar / Non Planar	Structure
$\text{Al}_2\text{Cl}_6$	$3c - 4e^-$	$sp^3 - sp^3 - sp^3$	Non Planar	 <p>(Driving force is to complete the octet)</p>
$\text{Al}_2\text{Br}_6$	$3c - 4e^-$	$sp^3 - sp^3 - sp^3$	Non Planar	
$\text{Be}_2\text{Cl}_4$	$3c - 4e^-$	$sp^2 - sp^3 - sp^2$	Planar	
$(\text{BeCl}_2)_n$ (solid)	$3c - 4e^-$	$sp^3 - sp^3 - sp^3$	Non Planar	
$\text{I}_2\text{Cl}_6$	$3c - 4e^-$	$sp^3d^2 - sp^3 - sp^3d^2$	Planar	
$\text{Fe}_2\text{Cl}_6$	$3c - 4e^-$	Not founded (we don't know)	Planar	
$\text{SnCl}_2$ (solid)	$3c - 4e^-$	$sp^3 - sp^3 - sp^3$	Non planar	 <p>(Driving force is to complete the octet)</p>

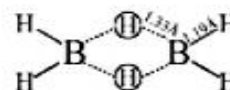
**Illustration**

1. The type of overlap in the bridge bond existing in  $\text{Al}_2(\text{CH}_3)_6$  is  
 (A)  $\text{sp}^3 - \text{sp}^3\text{d} - \text{sp}^3$  (B)  $\text{sp}^3 - \text{sp}^2 - \text{sp}^3$  (C)  $\text{sp}^3 - \text{s} - \text{sp}^3$  (D)  $\text{sp}^3 - \text{sp}^3 - \text{sp}^3$

Ans. (D)

**Exercise**

1. The molecular shapes of diborane is shown:  
 Consider the following statements for diborane:  
 1. Boron is approximately  $\text{sp}^3$  hybridised  
 2. B–H–B angle is  $180^\circ$   
 3. There are two terminal B–H bonds for each boron atom  
 4. There are only 12 bonding electrons available



Of these statements:

- (A) 1, 3 and 4 are correct (B) 1, 2 and 3 are correct  
 (C) 2, 3 and 4 are correct (D) 1, 2 and 4 are correct

Ans. (A)

**HYDROLYSIS**

Hydrolysis is a chemical process in which a certain molecule is split into two parts by the addition of a molecule of water. One fragment of the parent molecule gains a hydrogen ion ( $\text{H}^+$ ) from the additional water molecule. The other group collects the remaining hydroxyl group ( $\text{OH}^-$ ).

**Illustration**

1. Select correct statement about hydrolysis of  $\text{BCl}_3$  and  $\text{NCl}_3$   
 (A)  $\text{NCl}_3$  is hydrolysed and gives  $\text{HOCl}$  but  $\text{BCl}_3$  is not hydrolysed.  
 (B) Both  $\text{NCl}_3$  and  $\text{BCl}_3$  on hydrolysis gives  $\text{HCl}$   
 (C)  $\text{NCl}_3$  on hydrolysis gives  $\text{HOCl}$  but  $\text{BCl}_3$  gives  $\text{HCl}$ .  
 (D) Both  $\text{NCl}_3$  and  $\text{BCl}_3$  on hydrolysis gives  $\text{HOCl}$ .

Ans. (C)

**Exercise**

1. Which of the following halides cannot be hydrolysed?  
 (I)  $\text{TeF}_6$  (II)  $\text{SF}_6$  (III)  $\text{NCl}_3$  (IV)  $\text{NF}_3$   
 Choose the correct code :  
 (A) III & IV (B) I, II & III (C) I, II & IV (D) II & IV

Ans. (D)



<b>Compound</b>	<b>Mechanism</b>	<b>Hybridisation in Intermediate</b>	<b>Final Product or by product</b>	<b>No. of Water Molecule Utilised</b>	<b>Remark (Complete Hydro. partial H; Basicity (with respect to central atom)</b>
$\text{PCl}_3$	$[\text{SN}_2]_{\text{A}}$ & $[\text{SN}_2]_{\text{AE}}$	$\text{sp}^3\text{d}^2, \text{sp}^3\text{d}$	$\text{H}_3\text{PO}_4, \text{HCl}$	4	Complete H, Basicity = 3
$\text{SF}_4$	$[\text{SN}_2]_{\text{A}}$ & $[\text{SN}_2]_{\text{AE}}$	$\text{sp}^3\text{d}^2, \text{sp}^3\text{d}$	$\text{H}_2\text{SO}_3, \text{HF}$	3	Complete H, Basicity = 2
$\text{XeF}_4$	Disproportionation	—	$\text{Xe}, \text{O}_2, \text{XeO}_3$	1	—
$\text{IF}_7$	$[\text{SN}_2]_{\text{A}}$ & $[\text{SN}_2]_{\text{AE}}$	$\text{sp}^3\text{d}^3$	$\text{HIO}_4, 7\text{HF}$	4	Complete H, Basicity = 1
$\text{XeF}_6$	$[\text{SN}_2]_{\text{A}}$ & $[\text{SN}_2]_{\text{AE}}$	$\text{sp}^3\text{d}^3, \text{sp}^3\text{d}^2$	$\text{XeO}_3, 6\text{HF}$	3	Complete H
$\text{IF}_5$	$[\text{SN}_2]_{\text{A}}$ & $[\text{SN}_2]_{\text{AE}}$	$\text{sp}^3\text{d}^3, \text{sp}^3\text{d}^2$	$\text{HIO}_3, 5\text{HF}$	3	Complete H, Basicity = 1
$\text{ICl}$	$[\text{SN}_2]_{\text{A}}$	$\text{sp}^3\text{d}$	$\text{IOH}, \text{HCl}$	1	Complete H, Basicity = 1
$\text{ICl}_3$	$[\text{SN}_2]_{\text{A}}$ & $[\text{SN}_2]_{\text{AE}}$	$\text{sp}^3\text{d}^2, \text{sp}^3\text{d}$	$\text{HIO}_2, 3\text{HCl}$	2	Complete H, Basicity = 1
$\text{SO}_2\text{Cl}_2$	$[\text{SN}_2]_{\text{AE}}$	$\text{sp}^3\text{d}$	$\text{H}_2\text{SO}_4, 2\text{HCl}$	2	Complete H, Basicity = 2
$\text{SOCl}_2$	$[\text{SN}_2]_{\text{AE}}$	$\text{sp}^3\text{d}$	$\text{H}_2\text{SO}_3, 2\text{HCl}$	2	Complete H, Basicity = 2
$\text{POCl}_3$	$[\text{SN}_2]_{\text{AE}}$	$\text{sp}^3\text{d}$	$\text{H}_3\text{PO}_4, 3\text{HCl}$	3	Complete H, Basicity = 3
$\text{SeF}_4$	$[\text{SN}_2]_{\text{A}}$ & $[\text{SN}_2]_{\text{AE}}$	$\text{sp}^3\text{d}^2, \text{sp}^3\text{d}$	$\text{H}_3\text{SeO}_3, 4\text{HF}$	3	Complete H, Basicity = 2
$\text{TeF}_6$	$[\text{SN}_2]_{\text{A}}$	$\text{sp}^3\text{d}^3$	$\text{Te}(\text{OH})_6, 6\text{HF}$	6	Complete H, Basicity = 2
$\text{PCl}_3$	$[\text{SN}_2]_{\text{A}}$	$\text{sp}^3\text{d}$	$\text{P}(\text{OH})_3, 3\text{HCl}$	3	Complete H, Basicity = 2

Compound	Mechanism	Hybridisation in Intermediate	Final Product or by product	No. of Water Molecule Utilised	Remark (Complete hydro. partial H; Basicity (with respect to central atom))
$\text{BCl}_3$	$[\text{SN}_2]_{\text{A}}$	$\text{sp}^3$	$\text{B}(\text{OH})_3, 3\text{HCl}$ $[\text{B}(\text{OH})_4]^-$ in basic	3	Complete H, Basicity = 3
$\text{BeCl}_2$	$[\text{SN}_2]_{\text{A}}$	$\text{sp}^2$	$\text{Be}(\text{OH})_2, 2\text{HCl}$	2	Complete H, Basicity = 2
$\text{NCl}_3$	$[\text{SN}_2]_{\text{A}}$	$\text{Cl} \rightarrow \text{sp}^3\text{d}$	$3\text{HOCl}, \text{NH}_3$	3	Complete H
$\text{XeF}_2$	Redox	—	$\frac{1}{2} \text{Xe}, \text{HF}, 2 \text{O}_2$	1	—
$\text{H}_2\text{S}_2\text{O}_8$ (Marshall's acid)	$[\text{SN}_2]_{\text{AE}}$	$\text{sp}^3\text{d}$	$\text{H}_2\text{SO}_4, \text{H}_2\text{O}_2$	2	Complete H, Basicity = 2
$\text{P}_4\text{O}_{10}$	$[\text{SN}_2]_{\text{AE}}$	$\text{sp}^3\text{d}$	$\text{H}_3\text{PO}_4$	6	Complete H, Basicity = 3
$\text{H}_2\text{S}_2\text{O}_7$	$[\text{SN}_2]_{\text{AE}}$	$\text{sp}^3\text{d}$	$2\text{H}_2\text{SO}_4$	1	Complete H, Basicity = 2
$\text{P}_4\text{O}_6$	$[\text{SN}_2]_{\text{A}}$	$\text{sp}^3\text{d}$	$\text{H}_2\text{SO}_4$	6	Complete H, Basicity = 2
$\text{H}_4\text{P}_2\text{O}_6$	$[\text{SN}_2]_{\text{AE}}$	$\text{sp}^3\text{d}$	$\text{H}_3\text{PO}_4, \text{H}_2\text{O}_2$	2	Complete H, Basicity = 3
$\text{H}_2\text{SO}_5$	$[\text{SN}_2]_{\text{AE}}$	$\text{sp}^3\text{d}$	$\text{H}_2\text{SO}_4, \text{H}_2\text{O}_2$	1	Complete H, Basicity = 2
$\text{SiF}_4$	$[\text{SN}_2]_{\text{A}}$ lewis acid-base reaction	$\text{sp}^3\text{d}$	$\text{Si}(\text{OH})_4, 2\text{H}_2[\text{SiF}_6]$	4	Partial H, Basicity = 4
$\text{BF}_3$	$[\text{SN}_2]_{\text{A}}$ lewis acid-base reaction	$\text{sp}^3$	$\text{B}(\text{OH})_3, 3\text{H}[\text{BF}_4]$	3	Partial H, Basicity = 1

## MOLECULAR ORBITAL THEORY

VB (Valence bond theory) was unable to explain eg. Paramagnetic nature of  $O_2$  molecule, as per VBT ( $:O: :O:$ ), it should be diamagnetic.

### Definition:

The atomic orbital lose their identity during molecule formation (overlapping) and form new orbitals termed as molecular orbitals.

### Characteristic of molecular orbitals:

- (i) Molecular orbital formed by overlapping of atomic orbital of same energy
- (ii) Number of molecular orbital formed = number of atomic orbital involved in overlapping
- (iii) Half of the molecular orbital have lower energy are called Bonding molecular orbital.
- (iv) Half are of higher energy is termed as Antibonding molecular orbital
- (v) Electronic configuration in various molecular orbital are governed by same three rules.
  - (a) Aufbau's rule
  - (b) Hund's rule
  - (c) Pauli's exclusion principle

### Comparison of Bonding molecular orbital & Antibonding molecular orbital :

Bonding molecular orbital (BMO)	Antibonding Molecular orbital (ABMO)
Bonding MO is the result of the linear combination of AO when their wave function are added $\Psi_b = \Psi_A + \Psi_B$	ABMO is result of linear combination of AO when their wave function are subtracted $\Psi_a = \Psi_A - \Psi_B$
Generally it does not have node.	It always have a node between two nuclei of bonded atom.
Charge density increase between two nuclei resulting attraction between two atoms	Charge density decrease in between two nuclei, leads to repulsion between two atoms.
Energy of BMO is less, hence stable	Energy of ABMO is high, hence unstable

### Notation of molecular orbitals:

As atomic orbitals are known by letters s, p, d and f depending on their shapes. Similarly for molecular orbital.

For bonding molecular orbital-  $\sigma, \pi, \delta$  etc.

For antibonding molecular orbital-  $\sigma^*, \pi^*, \delta^*$  etc.

are used for different shapes of electron cloud.

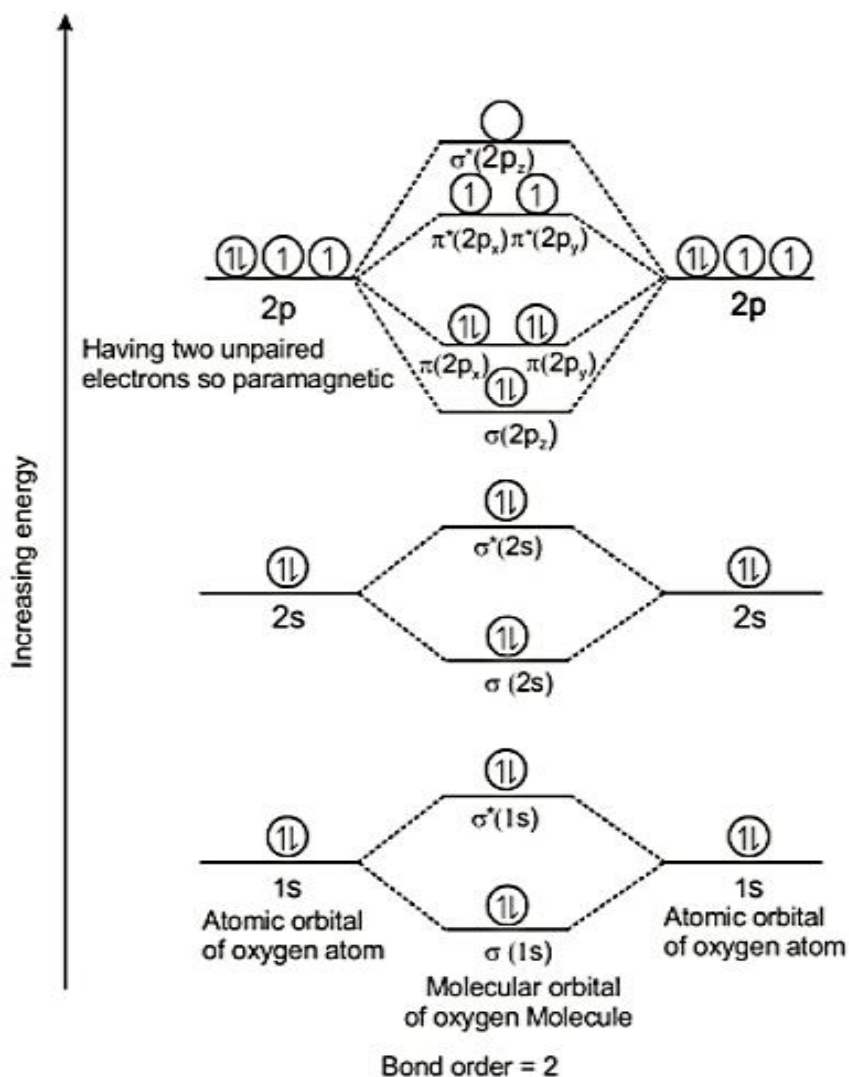
### Energy Level Diagram of molecular orbital :

On the basis of Aufbau's rule - increasing order of energies of various molecular orbitals is-

$$\sigma(1s) < \sigma^*(1s) < \sigma(2s) < \sigma^*(2s) < \sigma(2p_z) < \pi(2p_x) = \pi(2p_y) < \pi^*(2p_x) = \pi^*(2p_y) < \sigma^*(2p_z)$$

Energy level diagram for homonuclear diatomic molecules like,  $O_2$ ,  $F_2$ ,  $Ne_2$

For  $O_2$  molecule-



Bond order :  $O_2 = 2$

$O_2^+ = 2.5$

$O_2^- = 1.5$

$O_2^{2-} = 1.0$

Stability order –  $O_2^+ > O_2 > O_2^- > O_2^{2-}$

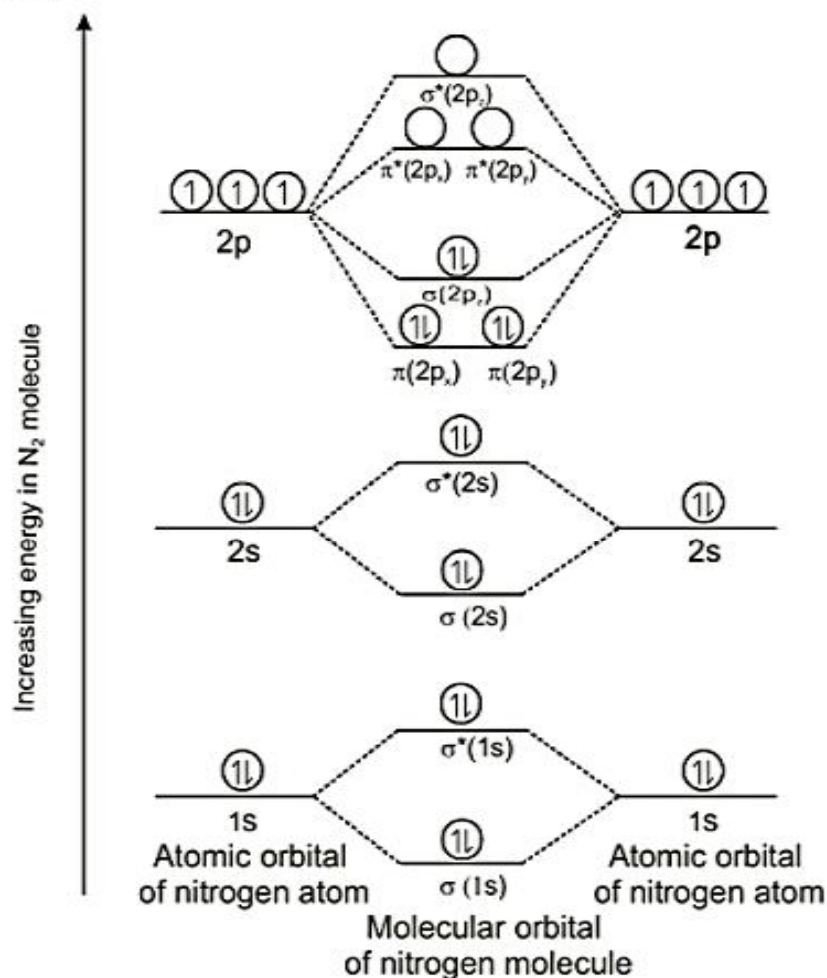
Bond length –  $O_2^{2-} > O_2^- > O_2 > O_2^+$



### Energy level diagram for $B_2$ , $C_2$ and $N_2$ molecules –

$$\sigma(1s) < \sigma^*(1s) < \sigma(2s) < \sigma^*(2s) < \pi(2p_x) = \pi(2p_y) < \sigma(2p_z) < \pi^*(2p_x) = \pi^*(2p_y) < \sigma^*(2p_z)$$

For  $N_2$  molecule



### Cause of exceptional behavior of molecular orbital in $B_2$ , $C_2$ and $N_2$ :

Energy of 2s and 2p atomic orbitals lie fairly close

Due to small energy difference between 2s and  $2p_z$  orbitals, the interaction between them is quite large.

This results in loss of energy by  $\sigma(2s)$  and  $\sigma^*(2s)$  and thus  $\sigma(2s)$  and  $\sigma^*(2s)$  becomes more stable at the cost of  $\sigma(2p_x)$  and  $\sigma^*(2p_x)$  which gets unstabilised (Higher energy).

### Electronic configuration of molecules and their related properties :-

For writing electronic configuration of diatomic molecules following two rules to be followed-

- Count the number of electrons present in two atoms and then fill in the appropriate energy level diagram according to Aufbau rule.
- The pairing in  $\pi(2p_x)$  and  $\pi(2p_y)$  or  $\pi^*(2p_x)$  and  $\pi^*(2p_y)$  will take place only when each molecular orbital of identical energy has one electron.
- After writing the molecular orbital diagram following parameter about molecules/ion may be predicted.

(i) **Bond order :-**

$$\text{Bond order} = \frac{1}{2} [N_b - N_a]$$

$N_b$  – Number of electron in bonding molecular orbital

$N_a$  – Number of electron in antibonding molecular orbital

(ii) **Bond length :-** (distance between two nuclei)  $\text{Bond length} \propto \frac{1}{\text{Bond order}}$ 

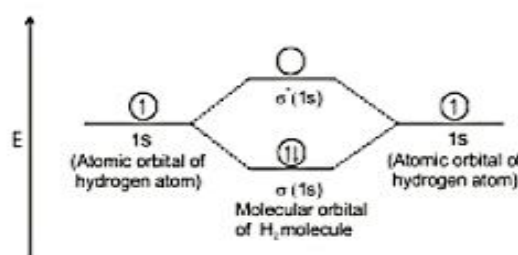
If  $N_b > N_a$  : then molecule exist

$\left. \begin{array}{l} N_b < N_a \\ N_b = N_a \end{array} \right\}$  Molecule does not exist

(iii) **Stability of molecules** - stability of molecule  $\propto$  Bond order of molecule(iv) **Dissociation energy** - Bond dissociation energy  $\propto$  Bond order(v) **Magnetic property** -

(a) When electron in Molecular orbital are paired – then the molecule is diamagnetic.

(b) When electron in Molecular orbital are unpaired – the molecule is paramagnetic.

**Bonding in molecules :-**(i) **Hydrogen molecule**- Having two H atoms with one electron each ( $1s$ )<sup>1</sup>

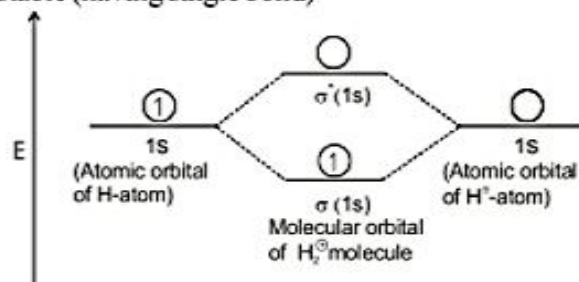
Molecular orbital (M.O.) configuration of  $H_2 = \sigma(1s)^2 \sigma^*(1s)^0$

$$\text{Bond order} = \frac{1}{2} [N_b - N_a]$$

$$= \frac{1}{2} [2 - 0] = 1 \text{ i.e. single bond}$$

Having paired electron, so diamagnetic.

Stability  $\rightarrow$  quite stable (having single bond)

(ii)  **$H_2^+$  ion –**

Molecular orbital (M.O.) configuration of Configuration of  $H_2^+ = \sigma(1s)^1 \sigma^*(1s)^0$

One electron in bonding molecular orbital.

So paramagnetic

$$\text{Bond order} = \frac{1}{2} [1 - 0] = \frac{1}{2}$$

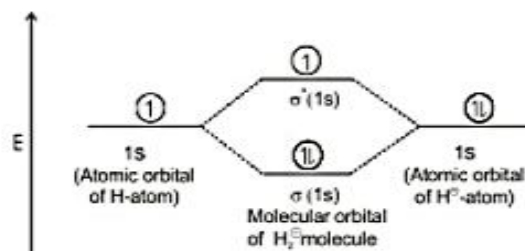
Less stable

(iii)  **$H_2^-$  anion -**

Molecular orbital (M.O.) configuration -  $\sigma(1s)^2 \sigma^*(1s)^1$

Paramagnetic

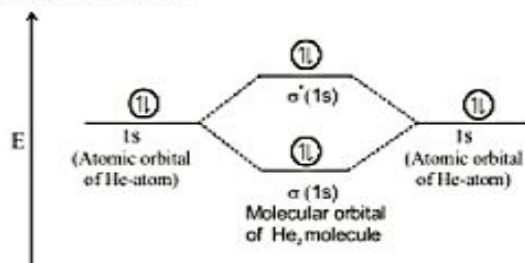
$$\text{Bond order} = \frac{1}{2} [2 - 1] = \frac{1}{2}$$



Stability is less than  $[H_2^+]$  because  $H_2^-$  contains antibonding molecular orbital (ABMO) electron

(iv) **Helium molecule ( $He_2$ )**: Molecular orbital (M.O.) configuration  $\sigma(1s)^2 \sigma^*(1s)^2$

- Diamagnetic
- Bond order =  $\frac{1}{2} [2 - 2] = 0$  (zero)
- Bond order zero indicates no linkage between He atoms. Hence  $He_2$  molecule does not exist
- Stability ( $He_2$ ) Highly unstable molecule



### Illustration

1. Comparison of CO &  $CO^+$  bond length on the basis of MOT.

**Sol.** CO is 14 electron system like  $N_2$ , have bond order three, highest energy electron in CO has slightly antibonding character due to energy difference in atomic orbital of C & O. So removing of an electron from CO decreases antibonding character so in  $CO^+$  bonding character increases therefore CO bond length in  $CO > CO^+$

### Exercise

1. During the formation of a molecular orbital from atomic orbitals, probability of electron density is:  
 (A) minimum in the nodal plane (B) maximum in the nodal plane  
 (C) zero in the nodal plane (D) zero on the surface of the lobe

**Ans.** (C)

2. Pick out the incorrect statement?  
 (A)  $N_2$  has greater dissociation energy than  $N_2^+$  (B)  $O_2$  has lower dissociation energy than  $O_2^+$   
 (C) Bond length in  $N_2^+$  is less than  $N_2$  (D) Bond length in  $NO^+$  is less than in NO.

**Ans.** (C)

3. Which of the following species is paramagnetic?  
 (A)  $NO^-$  (B)  $O_2^{2-}$  (C)  $CN^-$  (D) CO

**Ans.** (A)

4. Bond order of  $Be_2$  is:  
 (A) 1 (B) 2 (C) 3 (D) 0

**Ans.** (D)



**Characteristic of Covalent Compound :**

- (i) **Physical state :-** Covalent compounds are found in all the three states - Gas, Solid & Liquid.  
 Separate molecules – In gaseous state  
 Associate molecules – In liquid & solid state

(Due to strong vander waal's force and hydrogen bonding among the molecules.)

As the molecular weight increases, physical state changes :

eg.  $F_2$  and  $Cl_2$        $Br_2$        $I_2, At_2$   
                                  gas                   liquid                   solid



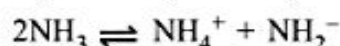
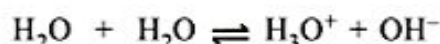
Top to bottom in a group, Vander waal's force increases between the molecules.

- (ii) **Covalent solid :** Those solids in which atoms are linked together by covalent bonds, forms infinite three dimensional giant structure. e.g. Diamond, Graphite,  $AlN$ ,  $SiC$ ,  $SiO_2$  etc.

**Molecular solid :** Discrete (separate) molecules are formed by covalent bonds and then the molecules associated due to intermolecular force of attraction. (Vander-waal's force)

eg. Solid  $I_2$ , dry ice (Solid  $CO_2$ ) etc.

- (iii) **Conductivity :** Mostly covalent compounds are bad conductor of electricity. But few polar covalent compounds due to self ionisation can conduct electricity.e.g.  $H_2O$ , liq.  $NH_3$  etc.



Free ions are formed which can conduct electricity.

**Exceptions : Graphite, HCl in water.**

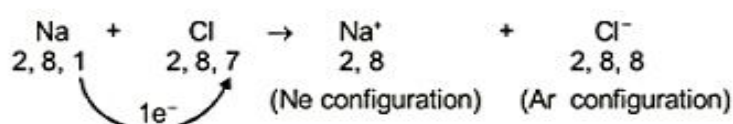
- (iv) **Solubility :** Non polar compound are soluble in non polar solvents. Non polar compounds forms Vander-waal's bond with non polar solvent molecules.
- (v) **Isomerism :** Covalent bond is rigid and directional, so it shows isomerism.  
 eg. Organic compounds.
- (vi) **Reaction :** Reaction between covalent compounds are slow. Because it involves breaking of old bonds and formation of new bonds

**ELECTROVALENT OR IONIC BOND**

- (i) The chemical bond formed between two or more atoms as a result of the complete transfer of one or more electrons from one atom to another is called **ionic or electrovalent bond**.
- (ii) Electro positive atom loses electron (group IA to IIIA)
- (iii) Electro negative atom gains electron (group VA to VIIA)
- (iv) Electrostatic force of attraction between cation and anion is called ionic bond or electrovalent bond.

Electronegativity difference  $\propto$  nature of ionic bond.

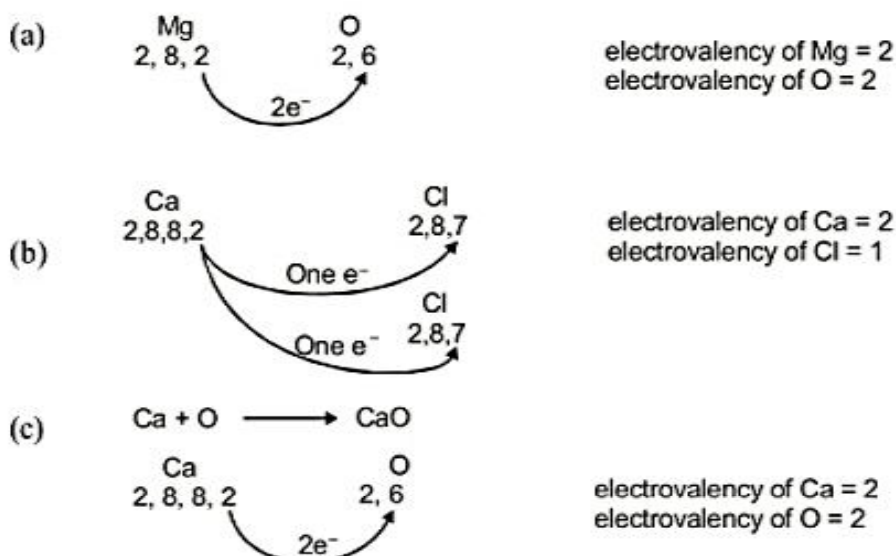
Example IA and VIIA group elements form maximum ionic compound.





- (v) More the distance between two elements in periodic table more will be ionic character of bond.  
 (vi) Total number of electron lose or gained is called electrovalency.

Example –



- (vii) The force of attraction is equal in all direction, so ionic bond is non-directional.  
 (viii) Ionic compound do not have molecular formula. It has only empirical formula. eg. NaCl is the empirical formula of sodium chloride.

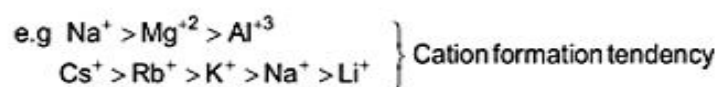
### Conditions for Forming Ionic Bonds :

Formation of Ionic bond depends upon these three factors :

(a) **Ionization energy :**

Amount of energy required to remove an electron from the outermost orbit of an isolated gaseous atom to form the positive ion or cation. (energy absorbed)

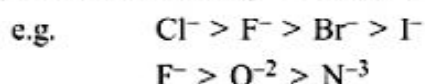
Lesser Ionisation energy → Greater tendency to form cation.



(b) **Electron affinity**

Amount of energy released when an electron is added to an isolated gaseous atom to form negative ion (i.e. : anion).

Higher electron affinity → Greater tendency to form anion



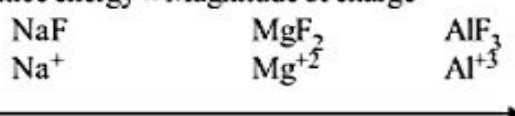
- (c) **Lattice energy** - Amount of energy released when one mole of crystal lattice is formed. Higher lattice energy → Greater will be the stability or strength of ionic compound.

**Factors affecting lattice energy :**

(i) **Magnitude of charge :**

Lattice energy (U)  $\propto z^+ z^-$  (Ionic charges of cation and anion)

Lattice energy  $\propto$  Magnitude of charge



- Lattice energy increases
- Size of cation decreases.

**(ii) Size of Cation :**

Lattice energy  $\propto \frac{1}{r^+ + r^-}$



- Size of cation increasing
- Size of anion is constant
- Lattice energy decreases

**Representation of formula of compounds :**

- (a) Write the symbols of the ions side by side in such a way that positive ion is at the left and negative ion is at the right as A<sup>+</sup>B<sup>-</sup>
- (b) Write their electrovalencies in figure at the top of each symbol as A<sup>x</sup>B<sup>y</sup>
- (c) Now apply criss cross rule as  $A^{\overset{x}{\cdot\cdot}}B^{\overset{y}{\cdot\cdot}}$ , i.e formula A<sub>y</sub>B<sub>x</sub>.

Examples : Calcium chloride  $Ca^{\overset{2}{\cdot\cdot}}Cl^{\overset{1}{\cdot\cdot}} = CaCl_2$

**Inert Pair Configuration**

The heavy elements of IIIA, IV A and V A groups form cations having charge equal to group number and two less than group number, e.g. Ti<sup>+3</sup>, In<sup>+1</sup>, Sn<sup>+2</sup>, Pb<sup>+2</sup>. In these elements due to more penetration power of s orbitals, the atom generally does not lose e<sup>-</sup> present in ns orbital, so only np electrons are lost by the atom. This effect is called “inert pair effect”.

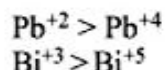
**Illustration**

1. Among the following, the element which show inert-pair effect are :

- |            |             |             |                 |
|------------|-------------|-------------|-----------------|
| (I) Bi     | (II) Sn     | (III) Pb    | (IV) C          |
| (A) I & II | (B) I & III | (C) II & IV | (D) I, II & III |

**Ans. (B)**

**Sol.** In a heavier p-block elements lower oxidation becomes more & more stable due to the inert pair effect. So the stability of



**Exercise**

1. Which of following stability order is incorrect due to inert pair effect.

- |  |   |   |   |
|--|---|---|---|
| (A) Hg <sup>0</sup> > Hg <sup>2+</sup> | (B) Bi <sup>3+</sup> > Bi <sup>5+</sup> | (C) Pb <sup>2+</sup> > Pb <sup>4+</sup> | (D) Fe <sup>2+</sup> < Fe <sup>3+</sup> |
|--|---|---|---|

**Ans. (D)**

## POLARIZATION

### (Fajan's Rule) (Covalent nature in ionic bond)

- When a cation approaches an anion closely the positive charge of a cation attracts the electron cloud of the anion towards itself, due to the electrostatic force of attraction between them.
- At the same time cation also repels the positively charged nucleus of anion.
- Due to this combined effect, cloud of anion is bulged or elongated towards the cation. This is called distortion, deformation or Polarization of the anion by the cation and anion is Polarized.

### Polarization Power :

The ability of cation to polarise a nearby anion is called Polarization power of cation.

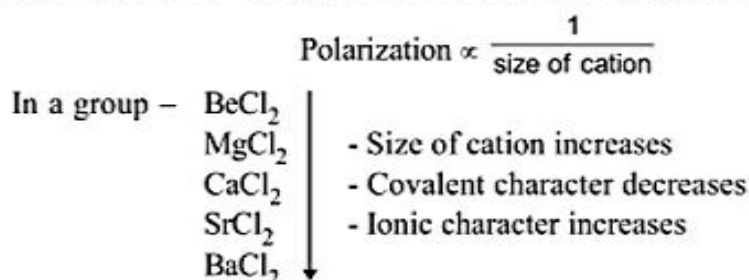


### Polarizability :

- Ability of anion to get polarised by the cation.
- Polarization of anion causes some sharing of electron between the ions so ionic bond acquires certain covalent character.
- Polarisation  $\propto$  Covalent-character
- Magnitude of polarization depends upon a number of factors, suggested by Fajan and are known as Fajan's rule.

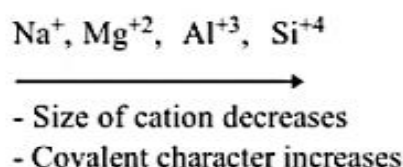
## FAJAN'S RULE : (FACTORS AFFECTING POLARIZATION)

- (a) **Size of cation :** - Polarization of the anion increases as the size of cation decreases.



Greatest polarizing power of Be<sup>2+</sup>, shows its maximum covalent character in BeCl<sub>2</sub>.

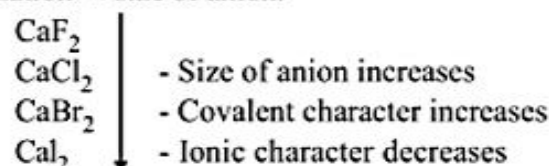
In a period –



- (b) **Size of anion**

If the size of the anion increases for a given cation, the covalent character increases

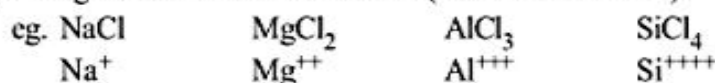
Polarization  $\propto$  size of anion.





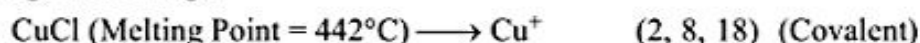
**(c) Charge on cation and anion :**

$\Rightarrow$  Polarisation  $\propto$  charge on cation / anion

**(I) Charge on cation  $\propto$  Polarisation (covalent character)**

- $\longrightarrow$
- Charge on cation increases
  - Covalent character increases
  - Ionic character decreases (Melting Point decreases)

$$\text{Charge on anion} \propto \text{polarisation} \propto \text{covalent nature} \propto \frac{1}{\text{Melting Point}}$$

**(d) Electronic configuration of cation :** If the size of cations in different compounds are same than that of cation having inert gas configuration, polarization capacity of cation having pseudo inert gas configuration is high.

Cu<sup>+</sup> and Na<sup>+</sup> both the cation (Pseudo & inert) have same charge and size but polarizing power of Cu<sup>+</sup> is more than Na<sup>+</sup> because  $Z_{\text{eff}}$  of ns<sup>2</sup>p<sup>6</sup> (inert) <  $Z_{\text{eff}}$  of ns<sup>2</sup>p<sup>6</sup>d<sup>10</sup> (pseudo).



So, CuCl has more covalent character than NaCl.

**Illustration**

1. Amongst LiCl, RbCl, BeCl<sub>2</sub> and MgCl<sub>2</sub>, the compounds with the greatest and the least ionic character, respectively are :

(A) LiCl and RbCl (B) RbCl and BeCl<sub>2</sub> (C) RbCl and MgCl<sub>2</sub> (D) MgCl<sub>2</sub> and BeCl<sub>2</sub>

**Sol.** (B)

According to the Fajans rule

$$\begin{aligned} \text{Covalent character} &\propto \text{polarisation power} \propto \frac{1}{\text{size of cation}} \\ &\propto \text{polarisability} \propto \text{size of anion} \end{aligned}$$

**Exercise**

1. The melting point of AlF<sub>3</sub> is 1291°C and that of SiF<sub>4</sub> is -77°C (it sublimes) because :
- (A) there is a very large difference in the ionic character of the Al-F and Si-F bonds
- (B) in AlF<sub>3</sub>, Al<sup>3+</sup> interacts very strongly with the neighbouring F<sup>-</sup> ions to give a three dimensional structure but in SiF<sub>4</sub> no such interaction is possible
- (C) the silicon ion in the tetrahedral SiF<sub>4</sub> is not shielded effectively from the fluoride ions whereas in AlF<sub>3</sub>, the Al<sup>3+</sup> ion is shielded on all sides
- (D) the attractive forces between the SiF<sub>4</sub> molecules are strong whereas those between the AlF<sub>3</sub> molecules are weak

**Ans.** (B)

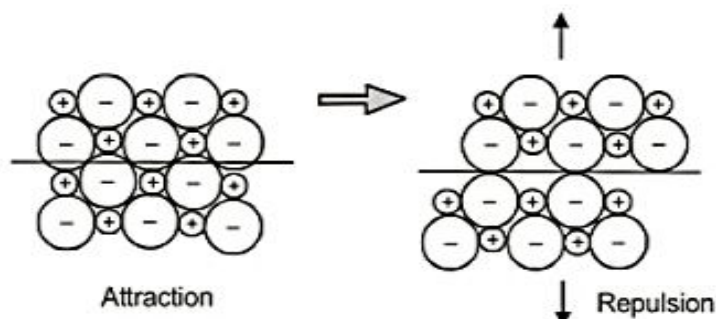


## Properties of ionic compounds :

### (a) Physical state :

Ionic compounds are hard, crystalline and brittle due to strong electrostatic force of attraction.

**Brittleness** →



(Same charged ions comes nearer. So they repel each other)

### (b) Isomorphism :

- Two compounds are said to be isomorphous if they have similar number of electrons i.e. similar electronic configuration of their cation and anion.
- They have similar crystal structure.

Example –	$\text{Na}^+$	$\text{F}^-$	$\text{Mg}^{+2}$	$\text{O}^{-2}$
Valency	+ 1,	-1	+ 2,	- 2
electronic configuration	2, 8,	2, 8	2, 8	2, 8
similarly	$\text{Ca}^{+2}$	$2\text{Cl}^{-1}$	$2\text{K}^{+1}$	$\text{S}^{-2}$
	(2, 8, 8)	(2, 8, 8)	(2, 8, 8)	(2, 8, 8)

### (c) Boiling point and melting point :

Ionic compounds have high boiling point and melting point due to strong electrostatics force of attraction among oppositely charged ions.

### (d) Conductivity :

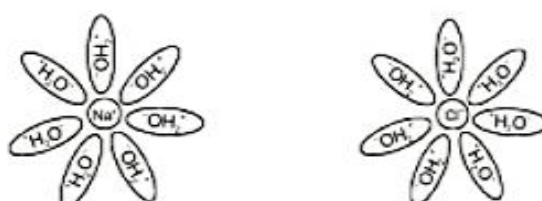
It depends on ionic mobility. In solid state - No free ions - Bad conductor of electricity.

In fused state or aqueous solution Due to free ions - Good conductor of electricity.

conductivity order : Solid state < Fused state < Aqueous solution.

### (e) Solubility : Highly soluble in water (Polar solvents) Example : NaCl in water

- The  $\text{Na}^+$  ions get associates with negatively charged 'O' of water
- And  $\text{Cl}^-$  ions associates with positively charged 'H' of water.



- (iii) Thus charge on  $\text{Na}^+$  and  $\text{Cl}^-$  decreases and electrostatics force of attraction also decreases which leads to free ion.
- (iv) The energy released due to interaction between solvent and solute is called solvation energy. If water is used as solvent it is called hydration energy.
- (v) For an ionic compound to be soluble in water  
Hydration energy > Lattice energy
- $$\text{Lattice energy} \propto \frac{1}{\text{Solubility}}$$
- $$\text{Hydration energy} \propto \text{Solubility.}$$
- $$\text{Hydration energy (H)} \propto \frac{1}{r_+} + \frac{1}{r_-} \quad \{r_+ \text{ \& } r_- \text{ are radius of cation and anion}\}$$
- (vi) Hydration energy mainly depends on the cation radius because the value  $\frac{1}{r_-}$  is negligible in comparison to  $\frac{1}{r_+}$ .
- (vii) Down the group both the lattice energy & hydration energy decreases, if decreases in lattice is greater than hydration energy, solubility increases down the group and vice versa.

### Illustration

1. The hydration of ionic compounds involves :  
 (A) Evolution of heat (B) Weakening of attractive forces  
 (C) Dissociation into ions (D) All of these
- Sol. (D) Theory Based

### Exercise

1. The correct order of hydration energy is  
 (A)  $\text{Be}^{+2} < \text{Li}^+$  (B)  $\text{Na}^+ > \text{Mg}^{+2}$  (C)  $\text{Na}^+ < \text{Mg}^{+2}$  (D)  $\text{Al}^{+3} < \text{Na}^+$
- Ans. (B)

### Factor affecting solubility :

#### (i) Dielectric constant :

The capacity of solvent to neutralise the charge of ionic compounds is called Dielectric constant. It is represented by " $\epsilon$ "

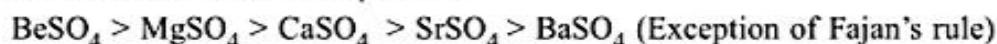
- (a) Water has maximum dielectric constant ( $\epsilon = 80$ )  
 $(\text{CH}_3\text{OH}, \epsilon = 35)$  ,  $(\text{Acetone}, \epsilon = 21)$   
 $(\text{C}_2\text{H}_5\text{OH}, \epsilon = 27)$  ,  $(\text{Ether}, \epsilon = 4.1)$   
 $(\text{Benzene}, \epsilon = 2.3)$   
 $\text{H}_2\text{O} > \text{CH}_3\text{OH} > \text{CH}_3\text{CH}_2\text{OH} > \text{CH}_3\text{COCH}_3 > \text{CH}_3\text{OCH}_3 > \text{C}_6\text{H}_6$
- (b) Ionic compounds are more soluble in the solvents, having high dielectric constant.
- (c)  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{O}_2$  have high dielectric constant but these are not a good solvent due to oxidising nature.

**(ii) Size of Ion :**

- (a) Keeping size of cation constant, the lattice energy decreases with the increases of anionic radius. Hence, order of solubility of LiX in water is  $\text{LiF} < \text{LiCl} < \text{LiBr} < \text{LiI}$

$$\text{As, solubility} \propto \frac{1}{\text{lattice energy}}$$

- (b) In LiI covalent nature is more according to Fajan's rule but Hydration Energy > Lattice Energy, therefore Li is more soluble in water.
- (c) Keeping size of anion constant, the hydration energy decreases with the increase of cationic radius. Hence order of solubility of  $\text{MSO}_4$  will be –



- (d) If size of cation and anion is very large, solubility decreases from top to bottom.
- (e) Solubility decreases in a period (as ionic nature decreases and covalent nature increases)
- $$\text{NaCl} > \text{MgCl}_2 > \text{AlCl}_3$$

**Illustration**

1. Which of the following is/are **incorrect** about solubility trend in group I & II?

	Least soluble in water	Most soluble in water
(A) Hydroxides	: LiOH	CsOH
(B) Carbonates	: $\text{Cs}_2\text{CO}_3$	$\text{Li}_2\text{CO}_3$
(C) Nitrate	: $\text{Ba}(\text{NO}_3)_2$	$\text{Be}(\text{NO}_3)_2$
(D) Sulphates	: $\text{BaSO}_4$	$\text{BeSO}_4$

Sol. (B)

Correct solubility order

**Exercise**

1. Choose the **correct code** for the following statements.

- I. The (–)ve value of  $\Delta H$  for the dissolution of ionic compound is enough to predict the compound is soluble in water at any temperature.
- II. For the alkali metals carbonate, solubility order decreases down the group.
- III. For the alkali metals ozonide, the thermal stability order increases down the group.
- IV. For the alkaline earth metals nitride, the thermal stability order increases down the group.

(A) T T F F

(B) T F F T

(C) T F T F

(D) F T T F

Ans. (C)

**DIPOLE MOMENT****(Ionic Nature in Covalent Bond)**

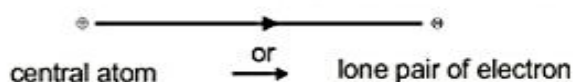
- (i) Polarity of any polar covalent bond or molecule is measured in terms of dipole moment.
- (ii) For measurement of extent of polarity, Pauling introduced the concept of dipole moment ( $\mu$ ).



The product of positive or negative charge ( $q$ ) and the distance ( $d$ ) between two poles is called dipole moment.

Here :  $\mu = q \times d$  (magnitude of charge  $\times$  distance)

- (iii) Dipole moment is a vector quantity i.e. it has both magnitude as well as direction.
- (iv) Direction of dipole moment is represented by an arrow pointing from electropositive to electronegative element and from central atom to lone pair of electrons.



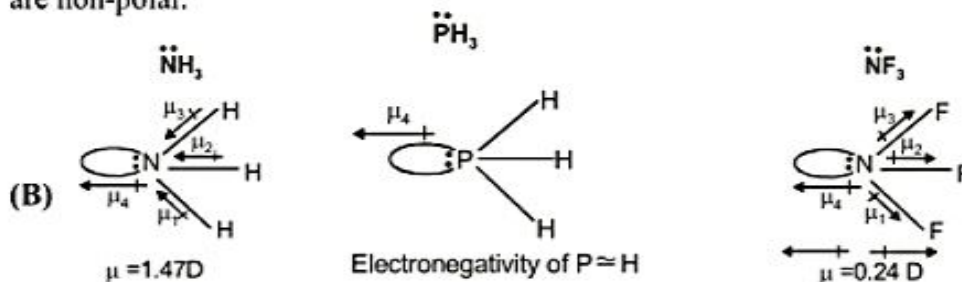
- (v) Unit of dipole moment is Debye

$$\begin{aligned} 1 \text{ Debye} &= 1 \times 10^{-18} \text{ esu cm.} \\ &= 3.33 \times 10^{-30} \text{ coulomb metre} \end{aligned}$$

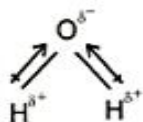
- (vi) In the diatomic molecule dipole moment ( $\mu$ ) depends upon difference of Electronegativity i.e. dipole moment ( $\mu$ )  $\propto$  **Electronegativity difference**  
order of dipole moment ( $\mu$ ) :  $\text{H-F} > \text{H-Cl} > \text{H-Br} > \text{H-I}$   
dipole moment ( $\mu$ ) = 0 for  $\text{H-H}$ ,  $\text{F-F}$ ,  $\text{Cl-Cl}$ ,  $\text{Br-Br}$ ,  $\text{O=O}$
- (vii) For polyatomic molecules dipole moments ( $\mu$ ) depends on the vector sum of dipole moments of all the covalent bonds.
- (viii) For  $\text{PCl}_5$  and  $\text{SF}_6$ , etc. dipole moment ( $\mu$ ) = 0 due to their regular geometry.
- (ix) Benzene, naphthalene, biphenyl have dipole moments ( $\mu$ ) = 0 due to planar structure.
- (x) If the vector sum is zero, than compound is non-polar compound or symmetrical compound (and it is not essential that individual dipole moments ( $\mu$ ) of every bond should be zero).

**Example : (A)**  $\text{BX}_3$ ,  $\text{CCl}_4$ ,  $\text{SiCl}_4$ ,  $\text{CH}_4$ ,  $\text{CO}_2$ ,  $\text{CS}_2$ ,  $\text{PCl}_5$ ,  $\text{SiH}_4$  etc.

In these examples the bond  $\text{B-F}$ ,  $\text{C-Cl}$ ,  $\text{C-H}$ ,  $\text{C-O}$ ,  $\text{P-Cl}$  etc. are polar even though compounds are non-polar.



- (xi) Dipole moment of  $\text{H}_2\text{O}$  is 1.85 D which is resultant dipole moment ( $\mu$ ) of two  $\text{O-H}$  bonds.



dipole moment ( $\mu$ ) of  $\text{H}_2\text{O}$  is more than dipole moment ( $\mu$ ) of  $\text{H}_2\text{S}$  because electronegativity of oxygen is higher than sulphur.

- (xii) Angular structure of molecule have greater dipole moment.

### Application of dipole moment :

- (i) **To determine polarity and geometry of molecule :**

If dipole moment ( $\mu$ ) = 0 compound is non polar and symmetrical

eg.  $\text{CO}_2$ ,  $\text{BF}_3$ ,  $\text{CCl}_4$ ,  $\text{CH}_4$ ,  $\text{BeF}_2$  etc.



If dipole moment ( $\mu$ )  $\neq 0$  compound will be polar and unsymmetrical.

eg.  $\text{H}_2\text{O}$ ,  $\text{SO}_2$ ,  $\text{NH}_3$ ,  $\text{Cl}_2\text{O}$ ,  $\text{CH}_3\text{Cl}$ ,  $\text{CHCl}_3$  etc.

(ii) To calculate % ionic character :

$$\% \text{ Ionic character} = \frac{\text{Experimental value of dipole moment}(\mu)}{\text{Theoretical value of dipole moment}(\mu)} \times 100$$

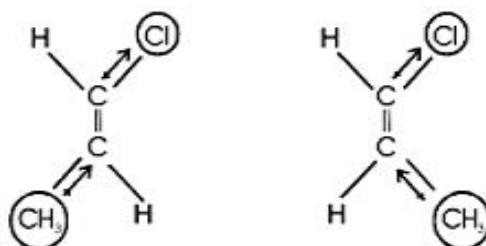
(iii) To distinguish cis form or trans form:-

(a) Dipole moment of cis isomers is normally higher than trans isomers.

eg. -



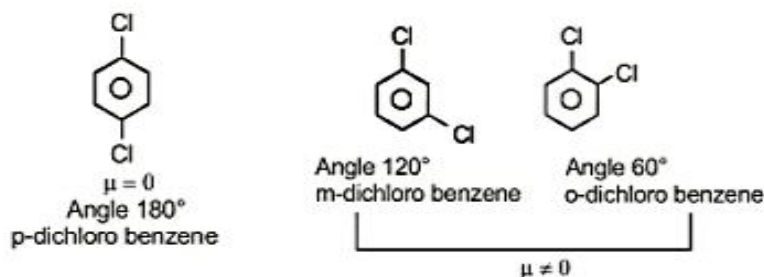
(b) If two groups have opposite inductive effect than trans-isomer will have greater dipole moment-  
eg.



(iv) To locate position of substituents in aromatic compounds.

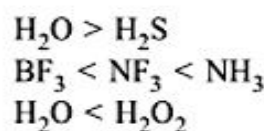
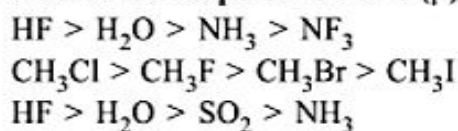
$$\text{Dipole moment}(\mu) \propto \frac{1}{\text{Bond angle}}$$

(a) If same substituents are present in the symmetrical position dipole moment ( $\mu$ ) of benzene ring compounds will be zero.



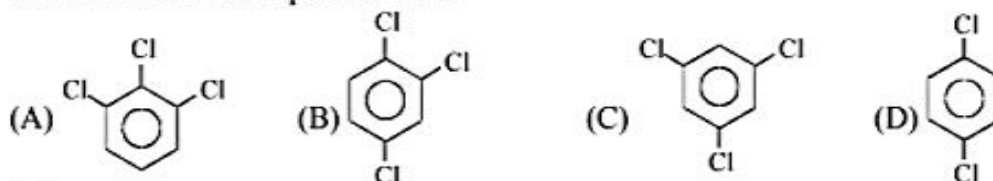
(b) As angle between substituents decrease value of dipole moment ( $\mu$ ) increase

Some important orders of dipole moments ( $\mu$ )



**Illustration**

1. Which has maximum dipole moment?



**Sol.** (A)  
Due to the symmetrical structure dipole moment of (C) & (D) are zero & (A) having maximum dipole moment.

**Exercise**

1. Which of the following has been arranged in order of decreasing dipole moment ?



**Ans.** (A)

2. The experimental value of the dipole moment of HCl is  $1.03 \text{ D}$ . The length of the  $\text{H}-\text{Cl}$  bond is  $1.275 \text{ \AA}$ . The percentage of ionic character in HCl is :



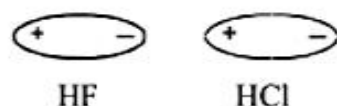
**Ans.** (C)

**VANDER WAAL'S FORCES**

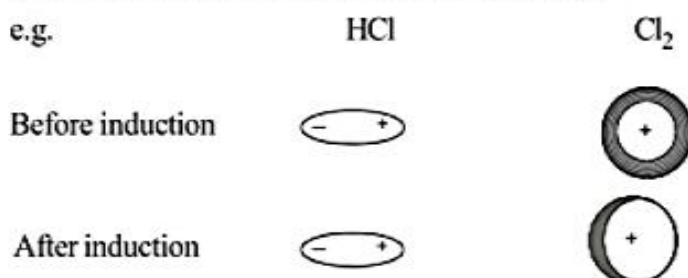
- (a) This type of attractive forces occurs in case of non-polar molecules such as  $\text{H}_2$ ,  $\text{O}_2$ ,  $\text{Cl}_2$ ,  $\text{CH}_4$ ,  $\text{CO}_2$  etc.  
(b) The existence of weak attractive forces among the non-polar molecule was first proposed by dutch scientist J.D. Vander Waal  
(c) Vander waal's force  $\propto$  molecular weight  
 $\propto$  Atomic weight  
 $\propto$  Boiling point

**Types of Vander Waal's force : -**

- (i) **Dipole-Dipole attraction or Keason force** - It is attraction in between two polar molecules such as HF and HCl

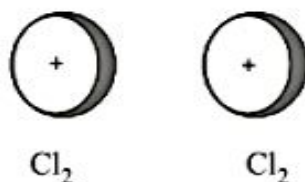


- (ii) **Dipole - Induced dipole attraction or Debye force** : In this case a neutral molecule is induced as a dipole by another dipole as shown in fig.



**(iii) Induced dipole - induced dipole attraction or London or dispersion force**

between two non polar molecules as in  $\text{Cl}_2$ , He etc.

**Illustration**

1. The strongest force among the following is

(A) London force                      (B) Ion-dipole interaction  
(C) Dipole-induced dipole interaction                      (D) Dipole-dipole interaction

Sol. (B)

For ion-dipole interaction

$$E \propto \frac{1}{r^2}$$

2. Select the correct statement :

(A) Boiling point of  $\text{NF}_3$  is greater than  $\text{NMe}_3$ .  
(B) Greater the dipole moments in molecule, greater will be the dipole-dipole interaction between the molecules.  
(C) London dispersion force increases with decreasing number of electrons.  
(D) Boiling point of hydrides of carbon family decreases down the group.

Sol. (B)

Surface area & molecular weight of  $\text{NMe}_3$  is greater than  $\text{NF}_3$ , so the boiling point of  $\text{NMe}_3 > \text{NF}_3$ .

**Exercise**

1. Xe can be liquified due to " \_\_\_\_\_ " with in molecules :

(A) ion-dipole interaction  
(B) dipole - dipole interaction  
(C) dipole - induced dipole interaction  
(D) instantaneous dipole - induced dipole interaction

Ans. (D)

**HYDROGEN BOND****Definition :**

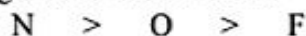
- (i) It is an electrostatic attractive force between covalently bonded hydrogen atom of one molecule and an electronegative atom (F, O, N)  
(ii) It is not formed in ionic compounds  
(iii) Hydrogen bond forms in polar covalent compounds, (not in non-polar)  
(iv) It is also known as dipole-dipole attraction or ion-dipole interaction.



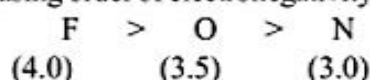
**Main condition for Hydrogen bonding :**

- (i) Hydrogen should be covalently bonded with high electronegative element like F, O, N  
 (ii) Atomic size of electronegative element should be small.

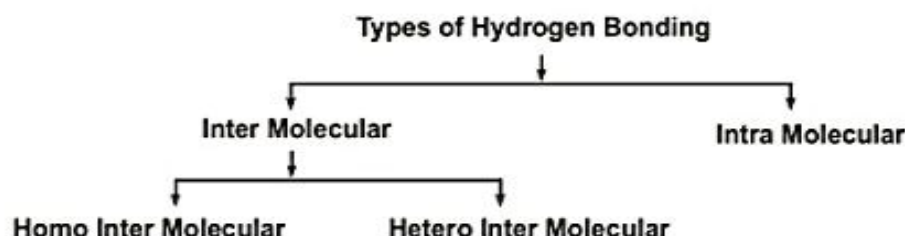
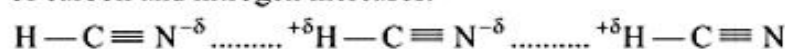
Decreasing order of atomic size is–



Decreasing order of electronegativity is –



- (iii) Strength of Hydrogen bond  $\propto$  Electronegativity of element  $\propto \frac{1}{\text{atomic size of element}}$   
 (iv) Hydrogen bonding occurs in HCN, due to ( $-\text{C} \equiv \text{N}$ ) triple bond (sp hybridisation), electronegativities of carbon and nitrogen increases.

**(A) Intermolecular Hydrogen bond**

Hydrogen bond formation between two or more molecules of either the same or different compounds known as **Inter molecular Hydrogen bonding**

These are two types.

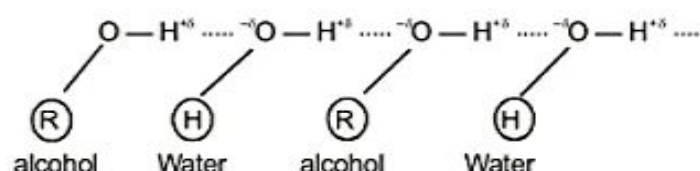
- (i) **Homointermolecular** :- Hydrogen bond between molecules of same compounds.

eg.



- (ii) **Heterointermolecular** :- Hydrogen bond between molecules of different compounds.

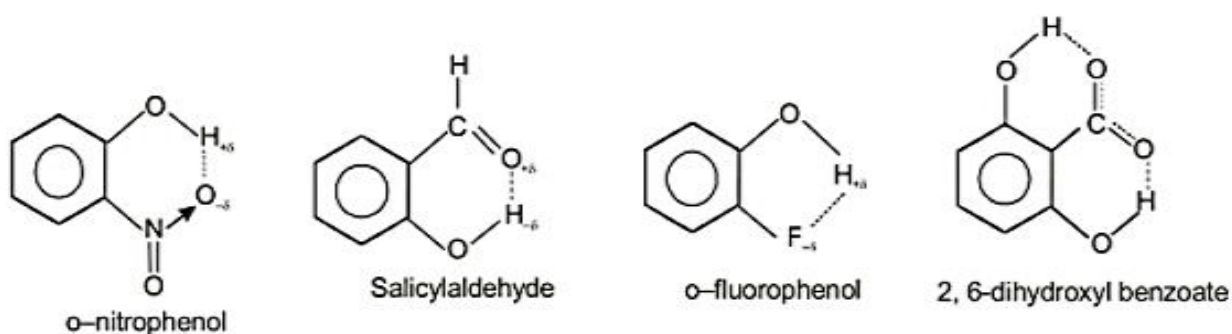
eg. alcohol, water

**(B) Intra molecular Hydrogen bond :-** It takes place within the molecule.

- (i) Hydrogen bonded with electronegative elements of a functional group, form Hydrogen bond with another electronegative element present on nearest position on the same molecule.  
 (ii) This type of Hydrogen bond is mostly occurred in organic compounds.  
 (iii) It result in ring formation (Chelation).



eg.

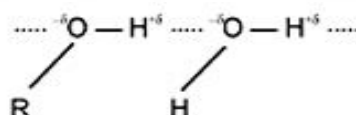


### Effect of Hydrogen bond on physical properties :

#### (i) Solubility :

##### (A) Inter molecular Hydrogen bonding

(a) Few organic compounds (Non-polar) are soluble in water (Polar solvent) due to Hydrogen bonding. eg. alcohol, acetic acid etc. are soluble in water.



Other examples—Glucose, Fructose etc, dissolve in water.

(b) Ketone, ether, alkane etc. are insoluble (no Hydrogen bond)

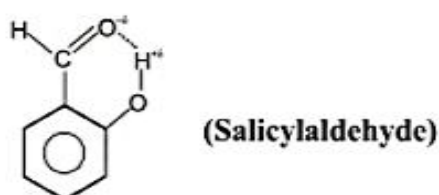
(c) Solubility order—  $\text{CH}_3\text{OCH}_3 < \text{CH}_3\text{OH}$

Primary amine > secondary amine > tertiary amine

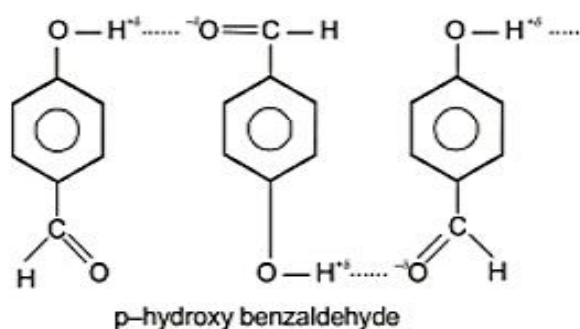
##### (B) Intra molecular Hydrogen bonding:

(a) It decreases solubility as it form chelate by Hydrogen bonding, so Hydrogen is not free for other molecule.

(b) It can not form H-bond with water molecule so can not dissolves.



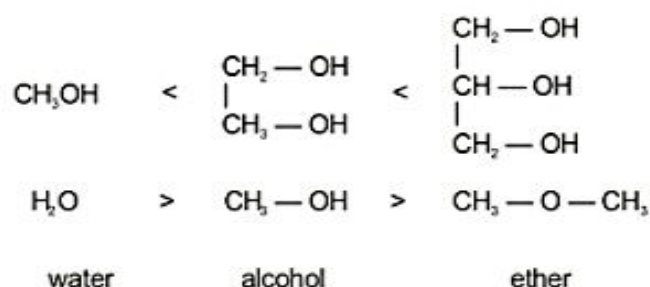
##### (C) Inter molecular Hydrogen bond



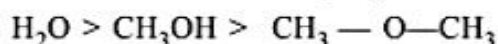
It can form Hydrogen bond with water molecule so it can dissolved

**(ii) Viscosity:**

Hydrogen bond associates molecules together, so viscosity increases

**(iii) Melting point and boiling point**

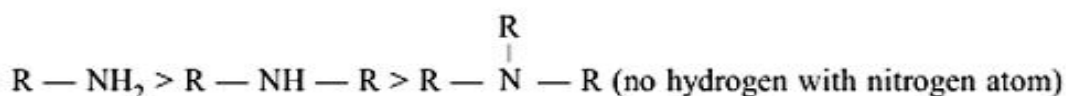
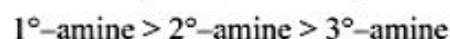
(a) Due to intermolecular Hydrogen bond Melting Point & Boiling Point of compounds increases.



(b) Trihydric alcohol > dihydric alcohol > monohydric alcohol

Monocarboxylic acid form stronger Hydrogen bond than alcohol of comparable molecular weight. Therefore Boiling Point of carboxylic acid is higher than alcohol.

(c) Decreasing order of Melting Point & Boiling Point isomer amines-



(d) Boiling points of VA, VIA, VIIA hydrides decreases on decreasing molecular weights.

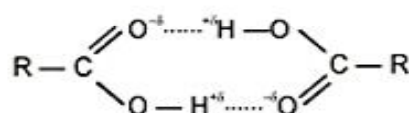
VA	VIA	VIIA	
NH <sub>3</sub>	H <sub>2</sub> O	HF	boiling point HF > HI > HBr > HCl
PH <sub>3</sub>	H <sub>2</sub> S	HCl	H <sub>2</sub> O > TeH <sub>2</sub> > SeH <sub>2</sub> > H <sub>2</sub> S
AsH <sub>3</sub>	SeH <sub>2</sub>	HBr	NH <sub>3</sub> > SbH <sub>3</sub> > AsH <sub>3</sub> > PH <sub>3</sub>
SbH <sub>3</sub>	TeH <sub>2</sub>	HI	

(e) But sudden increase in boiling point of NH<sub>3</sub>, H<sub>2</sub>O and HF is due to Hydrogen bonding



Intramolecular Hydrogen bonding gives rise to ring formation, so the force of attraction among these molecules are vander waal's force. So, Melting Point and Boiling Point are low.

**(iv) Molecular weight :** Molecular weight of CH<sub>3</sub>COOH is double of its molecular formula, due to dimer formation occur by Hydrogen bonding

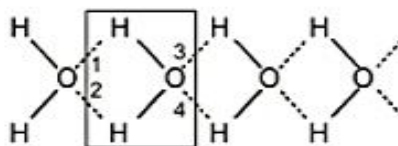


**(v) Physical state :** H<sub>2</sub>O is liquid while H<sub>2</sub>S is gas.

Water and Ice:- Both have Hydrogen bonding even then density of ice is less than water.

Volume of ice is more because of open cage like crystal structure, from by association of water molecules with the help of Hydrogen bond.

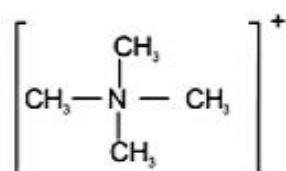
H<sub>2</sub>O becomes solid (Ice) due to four hydrogen bond among water molecule are formed in tetrahedral manner.



(vi) **Base strength**

CH<sub>3</sub>NH<sub>2</sub>, (CH<sub>3</sub>)<sub>2</sub>NH, (CH<sub>3</sub>)<sub>3</sub>N, form Hydrogen bond with water. So, less hydrolysis i.e. it gives OH<sup>-</sup> ions.

While (CH<sub>3</sub>)<sub>4</sub>N<sup>+</sup>OH<sup>-</sup> (ammonium compound) will give OH<sup>-</sup> ion in large amount due to no Hydrogen bonding.

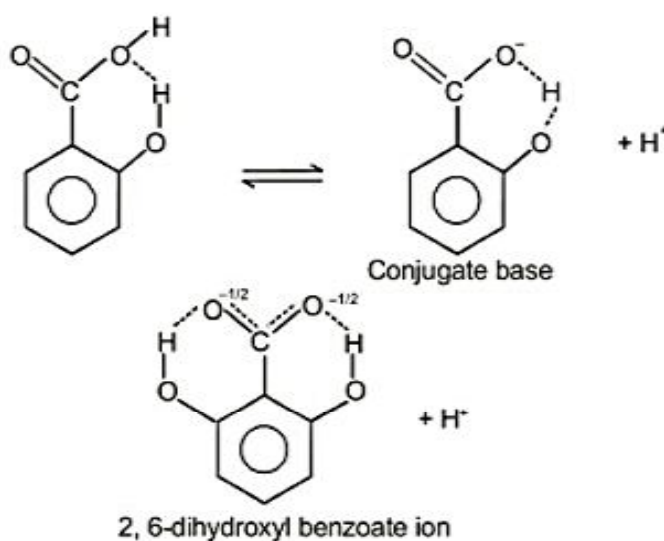


(Ammonium compound.)  
NO Hydrogen atom bonded directly with Nitrogen atom  
so no hydrogen bonding occurs.

**Effect of intramolecular H-bonding**

(i) **Strength of acid**

(a) The formation of intramolecular H-bonding in the conjugate base of an acid gives extra stability to conjugate base and hence acid strength increases eg. Salicylic acid is stronger than benzoic acid and 2, 6 – dihydroxy benzoic acid > salicylic acid.

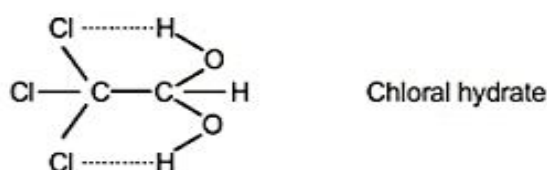
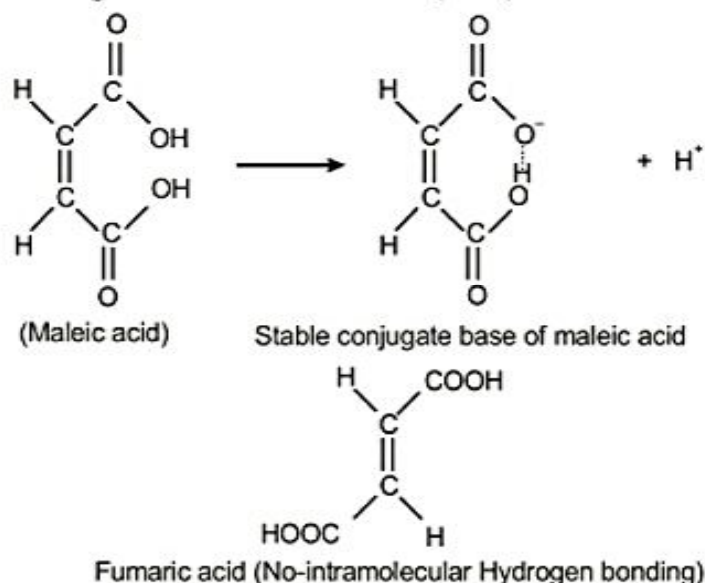


(b) C<sub>2</sub>H<sub>5</sub>SH is more acidic than C<sub>2</sub>H<sub>5</sub>OH. In C<sub>2</sub>H<sub>5</sub>OH, Hydrogen bond forms, so H<sup>+</sup> is not free

(c) HF is weaker acid than HI, due to Hydrogen bond in H – F, H<sup>+</sup> is not free

**(ii) Stability of chloral hydrate:-**

If two or more OH group on the same atom are present it will be unstable, but chloral hydrate is stable (due to Hydrogen bonding).

**(iii) Maleic acid (cis) is stronger acid than fumaric acid (trans).**

**Note:** The relative strength of various bonds is as follows

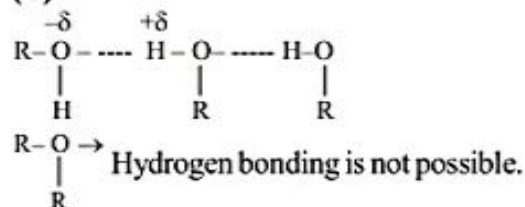
Ionic bond > Covalent bond > Metallic bond > Hydrogen bond > Vander waal's bond

**Illustration**

1. Ethanol has a higher boiling point than dimethyl ether though they have the same molecular weight. This is due to :

(A) resonance      (B) coordinate bonding (C) hydrogen bonding (D) ionic bonding

**Sol.** (C)

**Exercise**

1. Arrange the following in order of decreasing boiling point :

(I) *n*-Butane      (II) *n*-Butanol      (III) *n*-Butyl chloride      (IV) Isobutane

(A)  $IV > III > II > I$       (B)  $IV > II > III > I$       (C)  $I > II > III > IV$       (D)  $II > III > I > IV$

**Ans.** (D)



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## METALLIC BOND

- (a) The constituent particles of metallic solids are metal atoms which are held together by metallic bond.
- (b) In order to explain the nature of metallic bond Lorentz proposed a simple theory known as electron gas model or electron sea model.
- (c) A metal atom is supposed to consist of two parts, valence electrons and the remaining part (the nucleus and the inner shells) called kernel.
- (d) The kernels of metal atoms occupy the lattice sites while the space between the kernel is occupied by valence electrons.
- (e) Due to small ionization energy the valence electrons of metal atoms are not held by the nucleus firmly. Therefore, the electrons leave the field of influence of one kernel and come under the influence of another kernel. Thus the electrons are not localised but are mobile.
- (f) The simultaneous attraction between the kernels and the mobile electrons which hold the kernel together is known as metallic bond.

### Properties of metals and their explanation by electron sea model :

#### 1. Metallic lusture :

- (a) It is due to presence of delocalised mobile electrons
- (b) These loosely bonded electrons vibrate due to energy photon of incident light and radiates energy immediately.

#### 2. Electrical conductivity :

- (a) It is due to mobile electrons.
- (b) These electrons flow equally in all direction.
- (c) While applying a potential difference across a metal, there will be a directed flow of electrons towards the positive electrode.
- (d) The directed flow of electrons carries the electric current from one point to another and therefore, the metals are known to be good conductors.

#### 3. Thermal conductivity :

- (a) It can also be explained on the basis of electron gas model.
- (b) While heating a metal kinetic energy of electron increases and propagates through collisions.

#### 4. Malleability and ductility :

- (a) This property is due to non directional nature of metallic bond.
- (b) Basically the kernels can slip over each other when a deforming force is applied.

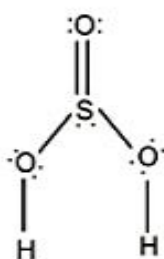
#### 5. High tensile strength :

It is due to positively charged kernels and the mobile valence electrons.

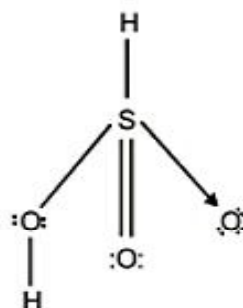
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## POINTS TO REMEMBER

- (a) Bond energy of a diatomic molecule is enthalpy change to dissociate one mole of the diatomic gaseous molecule to form the respective gaseous atoms.
- (b) Strong metallic bonding is favoured by smaller size of kernel.
- (c) Band theory is related with metallic nature
- (d) The resonance structure do not have independent existence.
- (e) The hydration of ionic compounds involves evolution of heat, weakening of attractive forces and dissociation into ions
- (f) The maximum covalency is equal to the actual number of s-electron and p-electrons in the outermost shell
- (g) Many ionic crystals dissolve in water because water decreases the interionic attraction in the crystal lattice due to solvation.
- (h) Hydrogen bond stabilizes the secondary structure of proteins.
- (i) Isoelectronic molecular species have similar molecular orbitals and similar structure according to isoelectric principle
- (j) The amount of energy required to break one mole of the bonded atom and separate the bonded atoms in the gaseous state is known as bond dissociation energy
- (k) The average angle between the bonded orbitals is known as bond angle ( $\theta$ ).
- (l) Bond length may be defined as the average distance between the centres of nuclei of two bonded atoms.
- (m) Polymorphism (Allotropy) is a term used when one and the same substance can crystallise in more than one forms.
- (n) In  $\text{SO}_2$ , there is  $p\pi - p\pi$  bonding as well as  $p\pi - d\pi$  bonding due to overlap of filled  $p\pi$  orbitals of oxygen with the vacant  $3d$  orbitals of sulphur.
- (o)  $\text{H}_2\text{SO}_3$  exists in two forms which are always in equilibrium with one another



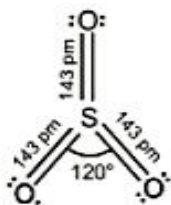
*(Symmetrical sulphurous acid)*



*(Unsymmetrical sulphurous acid)*

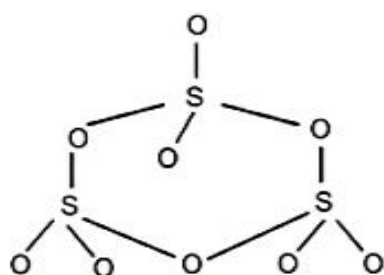
The unsymmetrical form containing S – H bond explains the reducing character of  $\text{H}_2\text{SO}_3$ .

- (p) The anion of  $\text{H}_2\text{SO}_3$  i.e.  $\text{SO}_3^{2-}$  has a pyramidal structure with S atom in  $\text{sp}^3$  hybridization and all the S – O bonds are of equal bond length (134 pm)
- (q) In the gaseous phase,  $\text{SO}_3$  is a planar triangular molecule with sulphur atom in  $\text{sp}^2$  hybridization state

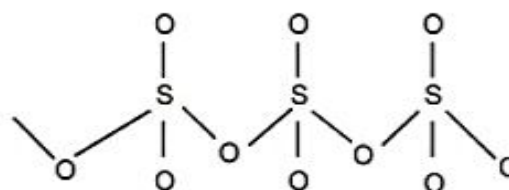


In order to account for the equivalency of all the S – O bonds and short S – O distance of 143 pm,  $\text{SO}_3$  may be considered as a resonance hybrid involving  $\text{p}\pi\text{-p}\pi$  S – O bonding along with additional  $\text{p}\pi\text{-p}\pi$  bonding.

- (r) In the solid phase,  $\text{SO}_3$  polymerizes to puckered rings or the more stable layer structure as shown.



Ring Structure



Layer Structure

## SOLVED EXAMPLES

**Q.1** An atom of element A has three electrons in its outer shell and B has six electrons in its outermost shell. The formula of the compound formed between these will be-

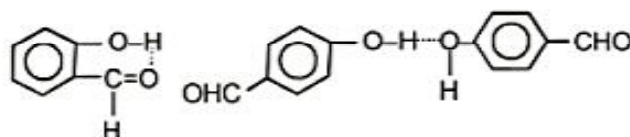
- (A)  $A_6B_6$                       (B)  $A_2B_3$                       (C)  $A_3B_2$                       (D)  $A_2B$

**Ans.** (B)

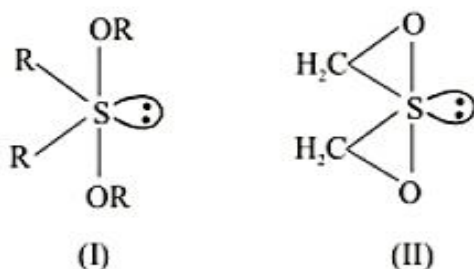
**Sol.** In this case the valence electron in the atom A is three and hence its valency is generally 3. In the atom B the number of valence electron is six. Hence its valency is usually 2. Hence the formula of the molecule formed from A and B could be  $A_2B_3$ . An example of two such elements are Al and O and the formula of Aluminium oxide is  $Al_2O_3$ .

**Q.2** o-Hydroxy benzaldehyde is a liquid at room temperature while p-hydroxy benzaldehyde is a high melting solid

**Sol.** o-Hydroxy benzaldehyde show intramolecular H-bonding or chelation, which are weaker than intermolecular H-bonding in p-hydroxy benzaldehyde.



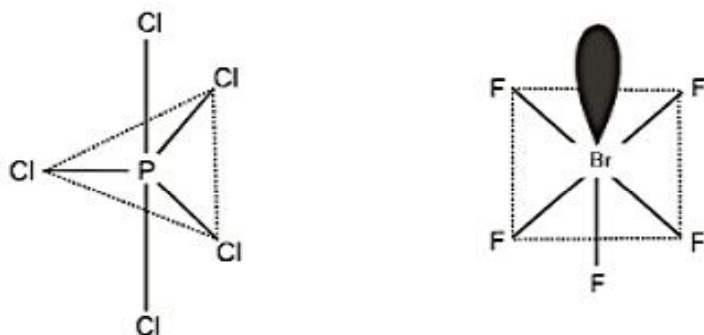
**Q.3** Compare the bond angle in (axial bond angle)



**Sol.** due to ring strain B.A. in second will be more than (I)

**Q.4** Using VSEPR theory, draw the shape of  $PCl_5$  and  $BrF_5$ .

**Sol.**



**Q.5** Indicate the type of hybridization of each carbon atom in the following compounds

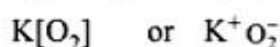
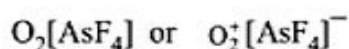
- (A)  $CH_3CN$                       (B)  $CH_3CH=CH_2$                       (C)  $H_3C-C\equiv C-CH_3$                       (D)  $HC\equiv C-CH=CH_2$

**Sol.** (A)  $sp^3$  and  $sp$                       (B)  $sp^3$ ,  $sp^2$ ,  $sp^2$                       (C)  $sp^3$ ,  $sp$ ,  $sp$ ,  $sp^3$                       (D)  $sp$ ,  $sp$ ,  $sp^2$ ,  $sp^2$



**Q.6** Among the following compounds/species write the order O–O bond length in  $O_2$ ,  $O_2[AsF_4]$ ,  $K[O_2]$

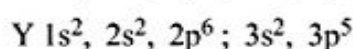
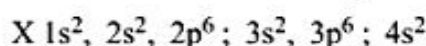
**Sol.**  $O_2$



The bond length decreases with increasing bond order

Species	$O_2$	$O_2^+$	$O_2^-$
Bond order	2.0	2.5	1.5
Bond length	$O_2^+$	$< O_2$	$< O_2^-$

**Q.7** Two elements X and Y have following electronic configuration-

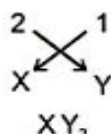


The expected compound formed by combination of X and Y will be expressed as-

- (A)  $XY_2$                       (B)  $X_5Y_2$                       (C)  $X_2Y_5$                       (D)  $XY_5$

**Ans.** (A)

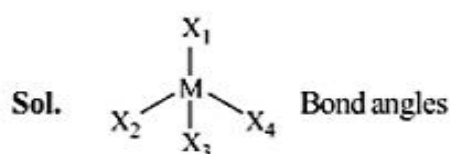
**Sol.** Valency of element X is 2 (2 electrons in the outermost shell) while that of element Y is 1 (1 electron required in the outermost shell to complete octet) So the formula of the compound between X and Y is  $XY_2$



**Q.8** The compound  $MX_4$  is tetrahedral. The number of  $< XMX$  angles in the compound is

- (A) Three                      (B) Four                      (C) Five                      (D) Six

**Ans.** (D)



Total angles are six [ $X_1MX_2$ ,  $X_1MX_3$ ,  $X_1MX_4$ ,  $X_2MX_3$ ,  $X_2MX_4$ ,  $X_3MX_4$ ]

**Q.9** The electronegativity of H and Cl are 2.1 and 3.0 respectively. The correct statement (s) about the nature of HCl is/are

- (A) 17% ionic                      (B) 83% ionic                      (C) 50% ionic                      (D) 100% ionic

**Ans.** (A)

**Sol.** % ionic character =  $16(X_A - X_B) + 3.5(X_A - X_B)^2$   
 $= 16(3.0 - 2.1) + 3.5(3.0 - 2.1)^2$   
 $= 14.4 + 2.83 = 17.235 \approx 17\%$

**Q.10** The electronegativity of O, F, N, Cl and H are 3.5, 4.0, 3.0, 3.0 and 2.1 respectively. The strongest bond will be :

- (A) F – O                      (B) O – Cl                      (C) N – H                      (D) O – H

**Ans.** (D)

**Sol.** Bond strength  $\propto$  Difference in electronegativity of atoms

**Q.11** In which solvent NaCl has maximum solubility

- (A)  $\text{H}_2\text{O}$  ( $\epsilon=80$ )              (B)  $\text{C}_2\text{H}_5\text{OH}$  ( $\epsilon=27$ )              (C)  $\text{CH}_3\text{COCH}_3$  ( $\epsilon=21$ ) (D)  $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$  ( $\epsilon=4.1$ )

**Ans.** (A)

**Sol.** Solubility  $\propto$  dielectric constant ( $\epsilon$ )

**Q.12** Which has maximum covalent character ?

- (A) NaCl                      (B)  $\text{SiCl}_4$                       (C)  $\text{AlCl}_3$                       (D)  $\text{MgCl}_2$

**Ans.** (B)

**Sol.** Polarisation in the molecule increases with increase of charge and decreases in size of the cation when the anion is same.

**Q.13** The dipole moment of HBr is  $2.6 \times 10^{-30}$  Cm and the interatomic spacing is 1.41 Å. The percentage of ionic character in HBr is-

- (A) 10.5                      (B) 11.5                      (C) 12.5                      (D) 13.5

**Ans.** (B)

**Sol.**              % ionic character =  $\frac{\text{Observed dipole moment}}{\text{Theoretical dipole moment}} \times 100$

Theoretical dipole moment of a 100% ionic character

$$= e \times d = (1.6 \times 10^{-19} \text{C}) \times (1.41 \times 10^{-10} \text{m})$$

$$= 2.256 \times 10^{-29} \text{ Cm}$$

$$\% \text{ ionic character} = \frac{2.6 \times 10^{-30}}{2.256 \times 10^{-29}} \times 100 = 11.5$$

**Q.14**  $\text{CO}_2$  is isostructural with

- (A)  $\text{CH}_4$                       (B)  $\text{SnCl}_2$                       (C)  $\text{HgCl}_2$                       (D)  $\text{NO}_2$

**Ans.** (C)

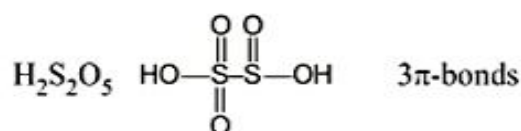
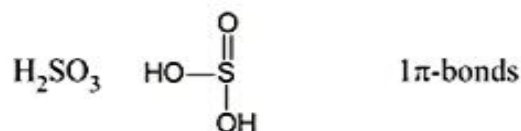
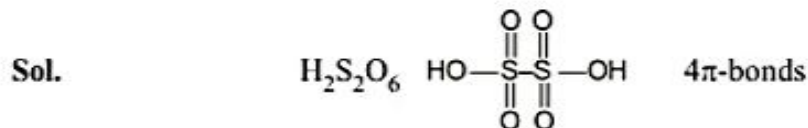
**Sol.** The structure of  $\text{CO}_2$  is linear  $\text{O}=\text{C}=\text{O}$ , similarly the structures of  $\text{HgCl}_2$  is linear ( $\text{Cl}-\text{Hg}-\text{Cl}$ ).  $\text{SnCl}_2$

and  $\text{NO}_2$  have angular structures and  $\text{CH}_4$  has tetrahedral structure  $\left( \begin{array}{c} \text{H} \\ | \\ \text{C} \\ / \quad \backslash \\ \text{H} \quad \text{H} \end{array} \right)$ .

**Q.15** Identify the correct sequence of increasing number of  $\pi$ -bonds in the structures of the following molecules:

- (I)  $\text{H}_2\text{S}_2\text{O}_6$                       (II)  $\text{H}_2\text{SO}_3$                       (III)  $\text{H}_2\text{S}_2\text{O}_5$   
(A) I, II, III                      (B) II, III, I                      (C) II, I, III                      (D) I, III, II

**Ans.** (B)

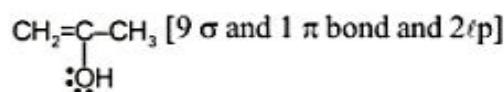


**Q.16** Enol form of acetone contains the following:

- (A) 9  $\sigma$ -bond, 1  $\pi$ -bond and two lone pair of electrons  
 (B) 8  $\sigma$ -bond, 2  $\pi$ -bond and two lone pair of electrons  
 (C) 10  $\sigma$ -bond, 1  $\pi$ -bond and one lone pair of electrons  
 (D) 9  $\sigma$ -bond, 2  $\pi$ -bond and one lone pair of electrons

**Ans.** (A)

**Sol.** Enol form of acetone is



**Q.17** The decreasing order of solubility of silver halide is

- (A)  $\text{AgI} > \text{AgBr} > \text{AgCl} > \text{AgF}$  (B)  $\text{AgF} > \text{AgCl} > \text{AgBr} > \text{AgI}$   
 (C)  $\text{AgCl} > \text{AgF} > \text{AgBr} > \text{AgI}$  (D)  $\text{AgBr} > \text{AgF} > \text{AgI} > \text{AgCl}$

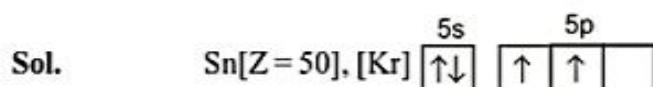
**Ans.** (B)

**Sol.**  $\text{AgI}$  has maximum covalent character [ $\because \text{I}^-$  is a large anion], while  $\text{AgF}$  has minimum covalent character, Therefore, it has more solubility

**Q.18** The atomic number of Sn is 50. The shape of gaseous  $\text{SnCl}_2$  molecule is :



**Ans.** (D)

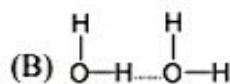
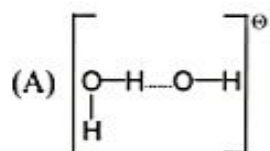


**Q.19** In which case hydrogen bond will not be observed

- (A)  $\text{H}_3\text{O}_2^-$  (B)  $\text{H}_2\text{O}$  (C)  $\text{H}_5\text{O}_2^+$  (D)  $\text{H}_3\text{O}^+$

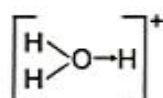
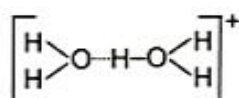
**Ans.** (D)

**Sol.**  $\text{H}_3\text{O}_2^-$  species



(C)  $\text{H}_5\text{O}_2^+$  (H-bonding)

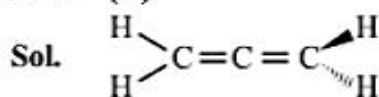
(D)  $\text{H}_3\text{O}^+$  (no H-bonding)



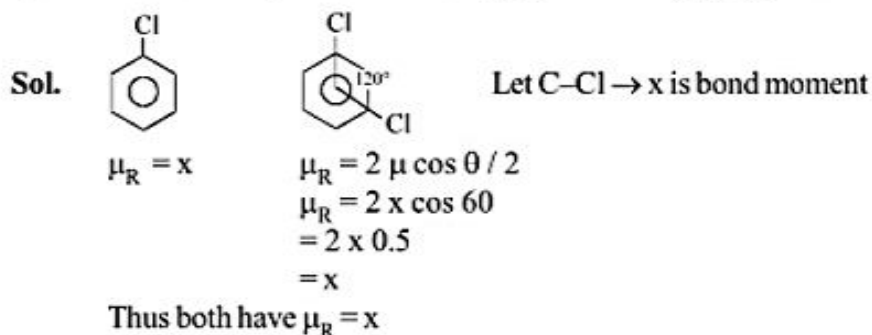
**Q.20** Which of the following statements is correct in the context of the allene molecule,  $\text{C}_3\text{H}_4$ ?

- (A) The central carbon is  $\text{sp}$  hybridized  
 (B) The terminal carbon atoms are  $\text{sp}^2$  hybridized  
 (C) The planes containing the  $\text{CH}_2$  groups are mutually perpendicular to permit the formation of two separate  $\pi$ -bonds.  
 (D) All correct

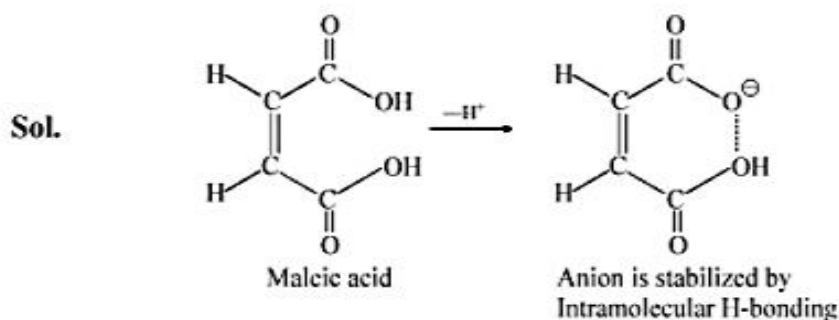
**Ans.** (D)



**Q.21** Prove that dipole moment of  $\text{C}_6\text{H}_5\text{Cl}$  and  $m\text{-C}_6\text{H}_4\text{Cl}_2$  are same.

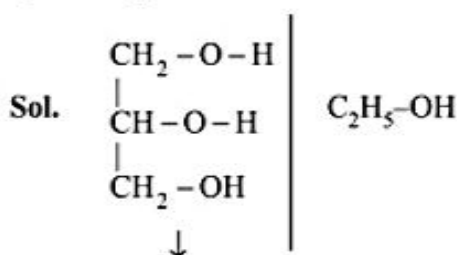


**Q.22** Maleic acid is more acidic than fumaric acid. Why?





**Q.23** Glycerol is more viscous than ethanol. Explain.



Due to presence of 3-OH groups higher no. of H-bonding, Glycerol is more viscous than ethanol.

**Q.24** It has been observed that % 's' character in Sb-H bond in  $\text{SbH}_3$  is 0.5%. Predict the % 's' character in the orbital occupied by the lone pair is.

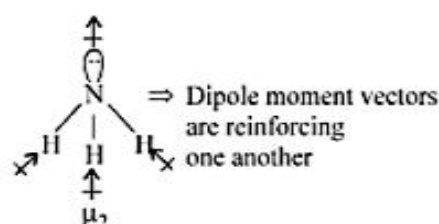
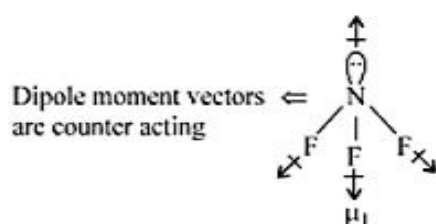
- (A) 99.5 %                      (B) 99.0 %                      (C) 98.5 %                      (D) 98.0 %

**Ans.** (C)

**Sol.** Total % s-character in three Sb-H bond pairs =  $0.5 + 0.5 + 0.5 = 1.5\%$   
hence % s-character in  $\ell.p.$  =  $100 - 1.5 = 98.5\%$

**Q.25** The dipole moment of  $\text{NH}_3$  is more than that of  $\text{NF}_3$

**Sol.**



$$\therefore \mu_1 < \mu_2$$

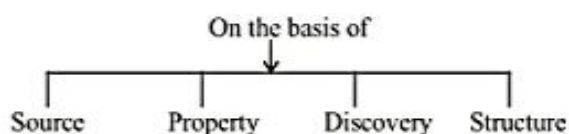
Also Polarity of  $\text{N} \text{---} \text{F}$  bond > Polarity of  $\text{N} \text{---} \text{H}$  bond  
(E.N = 3.0)    (E.N = 4.0)                      (E.N = 3.0)    (E.N = 2.1)

## NOMENCLATURE OF ORGANIC COMPOUNDS

Mainly three systems are adopted for naming an organic compound : –

- (i) **Common Names or Trivial System**
- (ii) **Derived System**
- (iii) **IUPAC system or Geneva System**

### COMMON OR TRIVIAL SYSTEM



(i) On the basis of source from which they were obtained.

S.No.	Organic Compound	Trivial Name	Source
1.	$\text{CH}_3\text{OH}$	Wood spirit or Methyl spirit	Obtained by destructive distillation of wood.
2.	$\text{NH}_2\text{CONH}_2$	Urea	Obtained from urine
3.	$\text{CH}_4$	Marsh gas (fire damp)	It was produced in marsh places.
4.	$\text{CH}_3\text{COOH}$	Vinegar	Obtained from Acetum - i.e. Vinegar
5.	$\begin{array}{c} \text{COOH} \\   \\ \text{COOH} \end{array}$	Oxalic acid	Obtained from oxalis plant.
6.	$\text{HCOOH}$	Formic acid	Obtained from formicus [Red ant]
7.	$\begin{array}{c} \text{CH}_3 - \text{CH} - \text{COOH} \\   \\ \text{OH} \end{array}$	Lactic acid	Obtained from lactous (milk)
8.	$\begin{array}{c} \text{CH}_2 - \text{COOH} \\   \\ \text{CH(OH)COOH} \end{array}$	Malic acid	Obtain from Apple
9.	$\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$	Butyric acid	Obtained from butter.
10.	$\text{CH}_3(\text{CH}_2)_4\text{COOH}$	Caproic acid	Obtained from goats.
11.	$\text{C}_2\text{H}_5\text{OH}$	Grain alcohol	Obtained from barley.

**(ii) On the basis of property**

- |   |                             |
|---|-----------------------------|
| 1. Glucose - Sweet in test              | 2. Glycol - Sweet poisonous |
| 3. Glycerol - Sweet<br>(Glycus - Sweet) |                             |

**(iii) On the basis of discovery**

- |                           |                                |
|---------------------------|--------------------------------|
| 1. RMgx (Grigard Reagent) | 2. $R_2Zn$ (Frankland reagent) |
|---------------------------|--------------------------------|

**(iv) On the basis of structure**

S.No.	No. of Carbon atom	Word Root
(i)	1C	Meth
(ii)	2C	Eth
(iii)	3C	Prop
(iv)	4C	But
(v)	5C	Pent
(vi)	6C	Hex
(vii)	7C	Hept
(viii)	8C	Oct
(ix)	9C	Non
(x)	10C	Dec

**Common Names for Hydrocarbon Derivatives**

S.No.	Compound	Name
1.	$R - X$	Alkyl halide
2.	$R - OH$	Alkyl alcohol
3.	$R - SH$	Alkyl thio alcohol
4.	$R - NH_2$	Alkyl amine
5.	$R-O-R$	Dialkyl ether
6.	$\begin{array}{c} R-C-R \\    \\ O \end{array}$	Dialkyl ketone
7.	$R-NH-R$	Dialkyl amine
8.	$\begin{array}{c} R-N-R \\   \\ R \end{array}$	Trialkyl amine
9.	$R-O-R'$	Alkyl alkyl' ether
10.	$\begin{array}{c} R-C-R' \\    \\ O \end{array}$	Alkyl alkyl' ketone
11.	$R-NH-R'$	Alkyl alkyl' amine
12.	$\begin{array}{c} R-N-R' \\   \\ R'' \end{array}$	Alkyl alkyl' alkyl'' amine

R is termed as alkyl -

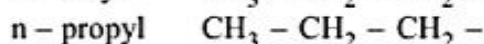
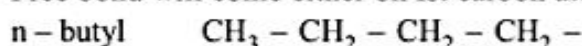
## GROUPS

Atom or a group of atoms which possess any 'free valency' are called as **Groups**.

If there are two structures of same molecular formula then some prefix (n, iso, neo) are used to differentiate them.

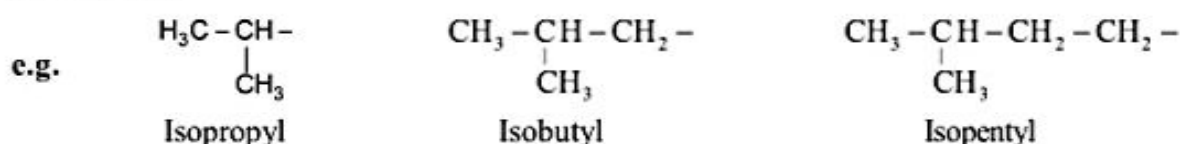
**Normal group : -**

- (a) It is represented by 'n'.
- (b) Groups having no branch (Straight chain).
- (c) Free bond will come either on 1st carbon atom or on last carbon atom.

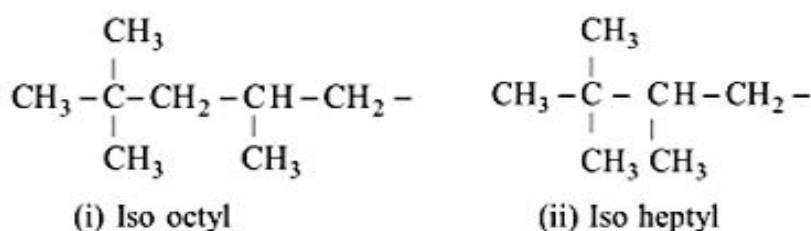


**Iso group : -**

When one methyl group is attached to the second last carbon of the straight carbon chain is named as iso group.

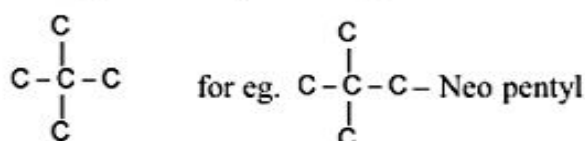


**Exception :**



**Neo group : -**

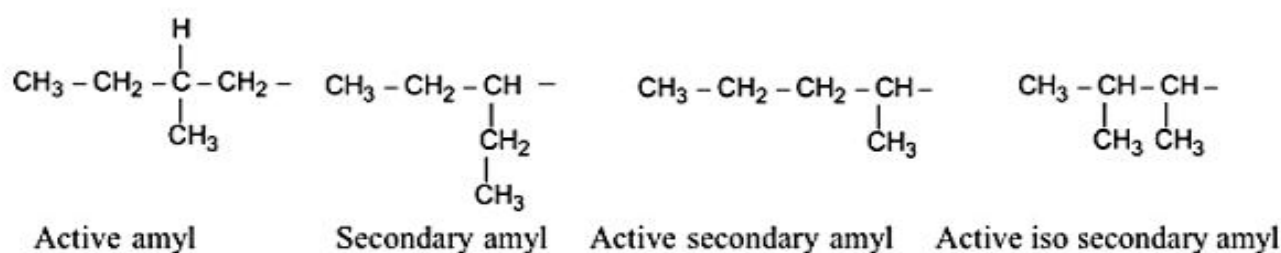
- (a) When two methyl groups on second last carbon of a straight carbon chain is attached to other four carbon atom group is named as neo group.
- (b) It is represented by following structure -



- (c) There should be one 4° carbon and at least three methyl group on 4° carbon.

**NOTE :** (Optically Active) = If all valency are attached to different atoms.

**Amyl group : -**

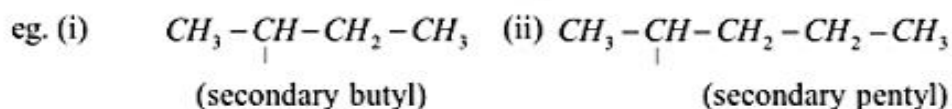




**Secondary group : –**

(a) The carbon having free valency attached to two carbon is called secondary carbon.

(b) It is represented by following structure.  $C - \underset{|}{C} - C - C$

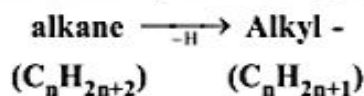
**Tertiary group : –**

(a) The carbon having free valency attached to three other carbon .

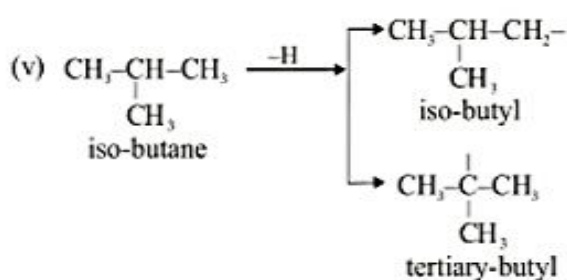
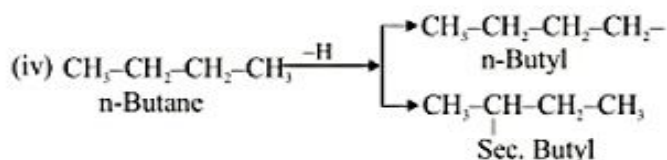
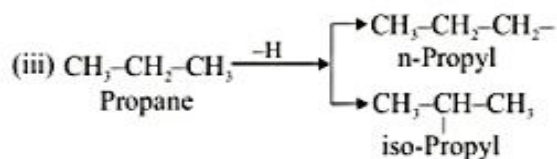
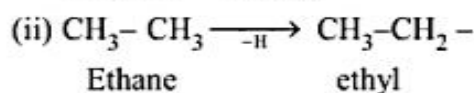
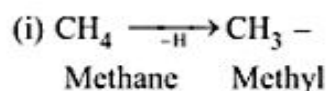
(b) It is represented by following structure -  $\begin{array}{c} C \\ | \\ C - C - C \\ | \end{array}$

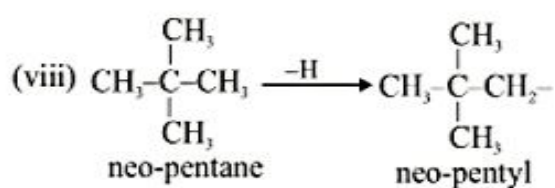
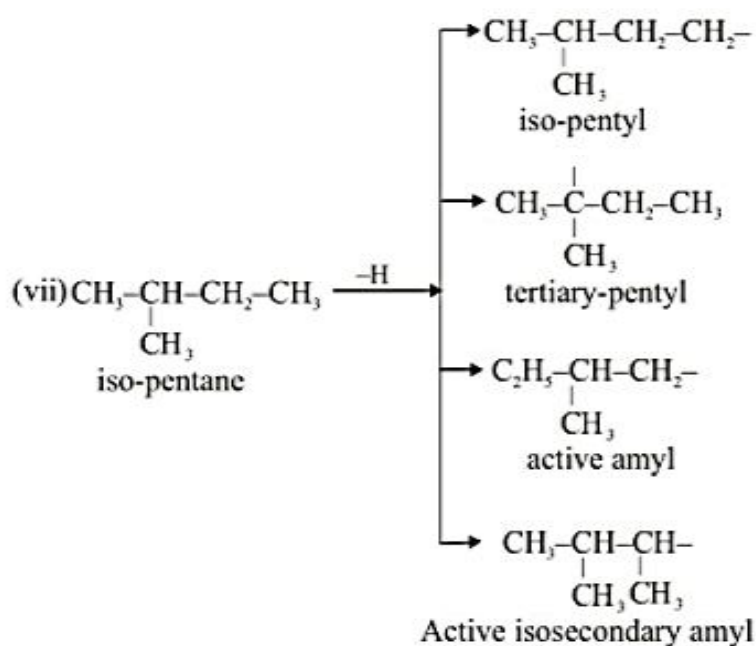
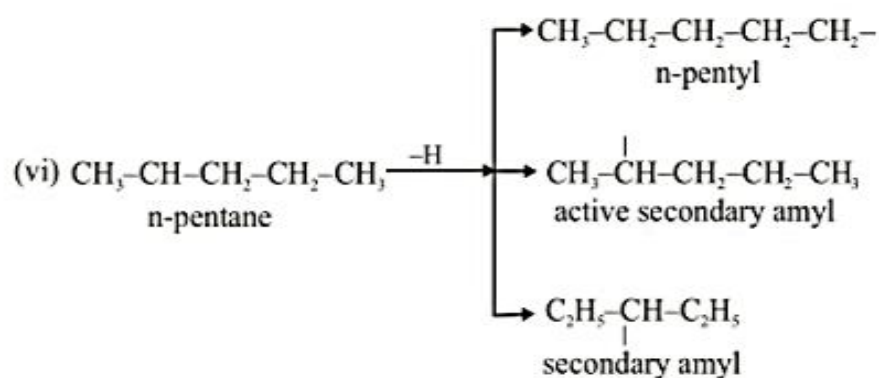
**Alkyl group : –**

When a hydrogen is removed from Alkane (saturated hydrocarbon) then alkyl group is formed. A bond is vacant on alkyl group on which any functional group may come.

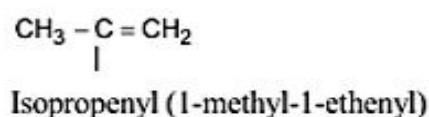
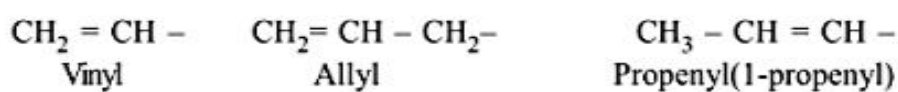
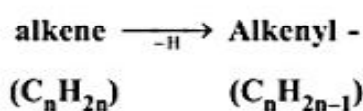


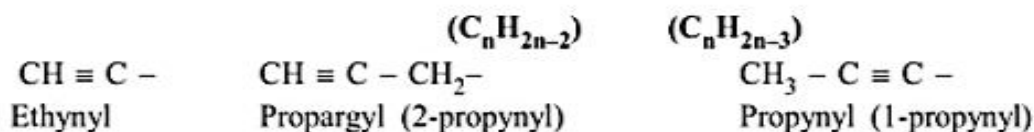
e.g.



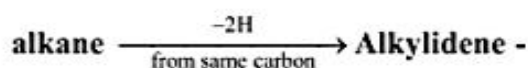


**Alkenyl group : –**

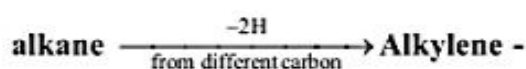




**Alkylidene group –**

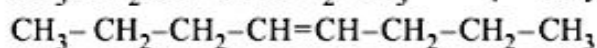
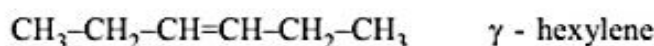
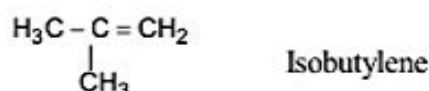
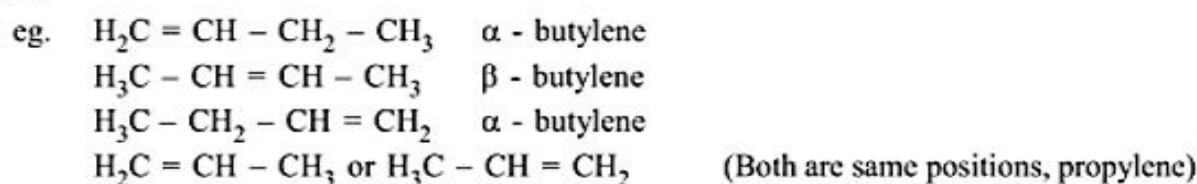


**Alkylene group**



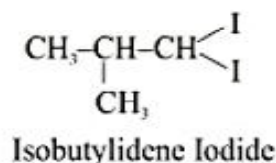
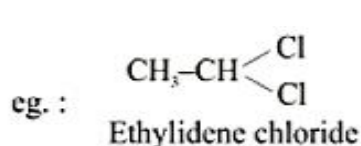
**Position of double bond : –**

In an unsaturated hydrocarbon if the position of double bond is on 1<sup>st</sup> or last carbon then it's prefix will be  $\alpha$  (alpha) if it is on 2<sup>nd</sup> carbon it is termed as  $\beta$  (Beta) & the  $\gamma$  (gamma) &  $\delta$  (delta) and so on.

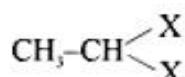


### COMMON - NAMING OF DIHALIDES

- When two same halogen atoms are attached to the same carbon such compounds are called **Gemdihalides**.
- Common names of such compounds are alkylidene halides



Exception : Methylidene halide (wrong)



Methylene halide (right)

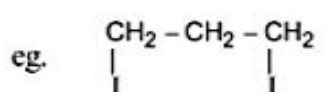
- (c) When two same halogen atoms are attached to adjacent carbon, these are called as vicinal dihalides. Common names of such compounds are alkylene halide.



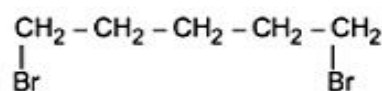
- (d) When two same halogen atoms are attached at the two ends of a carbon chain its common naming will be polymethylene halide.

'poly' word indicates the number of  $-\text{CH}_2-$  groups.

$-\text{CH}_2-$       2      3      4      5      6  
Poly      di      tri      tetra      penta      Hexa



Trimethylene Iodide



Pentamethylene Bromide

**Exception : -**

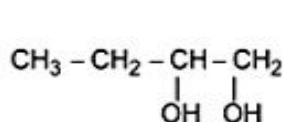
$\text{CH}_2 - \text{X}$  dimethylene halide (wrong)

|

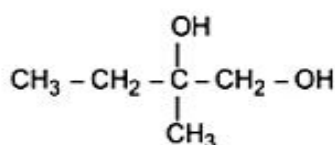
$\text{CH}_2 - \text{X}$  ethylene halide (right)

## COMMON - NAMING OF DI-HYDROXY COMPOUNDS

- (a) When two  $-\text{OH}$  groups are attached to adjacent carbon atoms they are termed as alkylene glycol.



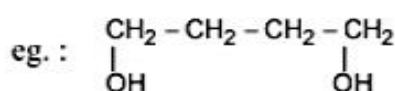
Butylene glycol



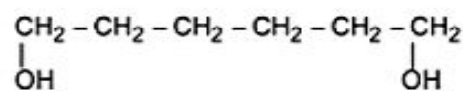
Active amylen glycol

- (b) When two  $-\text{OH}$  group are attached at the two ends of a carbon chain, these compounds are named as polymethylene glycol.

Poly  $\rightarrow$  Number of  $\text{CH}_2$  groups.



Tetra methylene glycol



Hexamethylene glycol

**Exception :**

$\text{CH}_2 - \text{OH}$  Dimethylene glycol (wrong)

|

$\text{CH}_2 - \text{OH}$  Ethylene glycol (right)

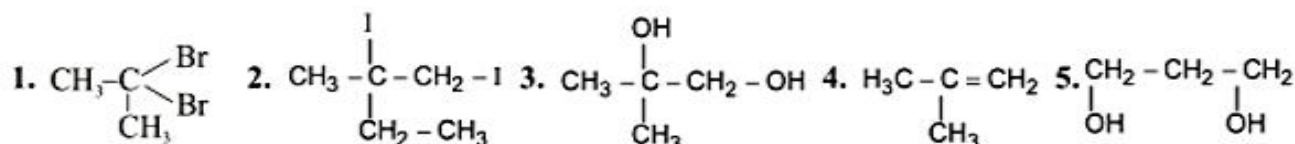


### PROBLEMS

Make the structure of following organic compounds -

- |                           |                          |                        |
|---------------------------|--------------------------|------------------------|
| 1. Isopropylidene Bromide | 2. Active amylene Iodide |                        |
| 3. Isobutylene glycol     | 4. Isobutylene           | 5. Trimethylene glycol |

### ANSWERS



## COMMON-NAMING OF THE FUNCTIONAL GROUP HAVING CARBON

(Common naming for Hydrocarbon derivatives)

S.No.	Functional group	Suffix
(i)	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{OH} \end{array}$	-ic Acid
(ii)	$\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ -\text{C}-\text{O}-\text{C}- \end{array}$	-ic anhydride
(iii)	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{O}-\text{R} \end{array}$	-ate
(iv)	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{NH}_2 \end{array}$	-amide
(v)	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{X} \end{array}$	-yl halide
(vi)	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{H} \end{array}$	-aldehyde
(vii)	$-\text{C} \equiv \text{N}$	-o-nitrile
(viii)	$-\text{N} \equiv \text{C}$	-o-isonitrile

**Prefix : -**

1 Carbon → Form-

2 Carbon → Acet-

3 Carbon → Propion-

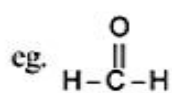
4 Carbon → Butyr  $\begin{array}{l} \rightarrow \text{Normal} \\ \rightarrow \text{Iso} \end{array}$  -

5 Carbon →

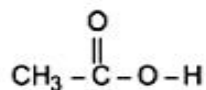
Valer  $\begin{array}{l} \rightarrow \text{Normal-} \\ \rightarrow \text{Iso-} \\ \rightarrow \text{Secondary-} \\ \rightarrow \text{Tertiary-} \end{array}$

3 C + (=) double bond = Acryl-

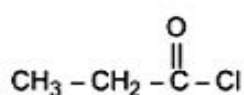
4 C + double bond = Croton-



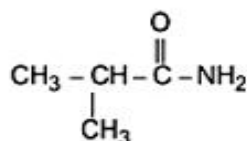
Formaldehyde



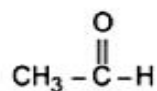
Acetic Acid



Propionyl chloride

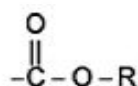


Isobutyramide

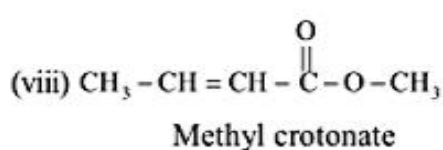
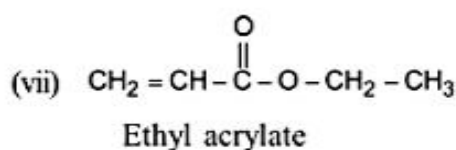
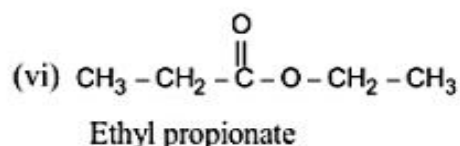
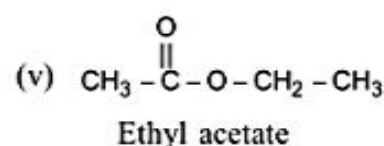
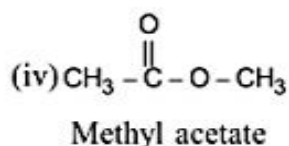
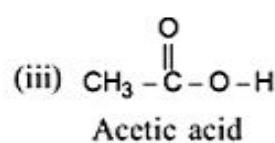
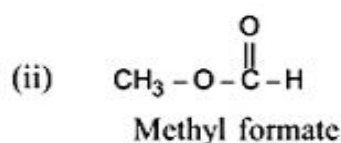
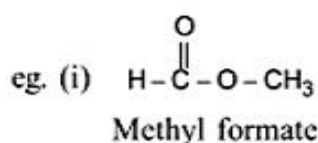


Acetaldehyde

## NOMENCLATURE OF ESTER



The group which is attached to the oxygen is written as alkyl & the remaining structure is named on the basis of Functional Group suffix.



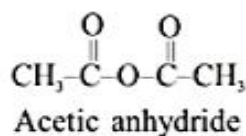
## NOMENCLATURE OF ANHYDRIDE

**Rule :** – Add the total number of carbon atoms & divide it by 2, the substract will give you the number of C - atom. Now name it according to suffix use for anhydride.

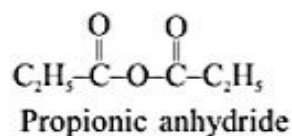
$$\frac{\text{Total}}{2} = \text{Substract}$$

$$= \text{Number of C atom}$$

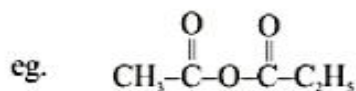
$$\frac{4}{2} = 2$$



$$\frac{6}{2} = 3$$



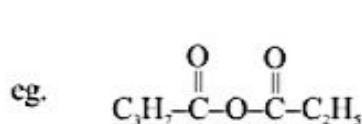
If  $R \neq R'$ , You need not to find out substract.



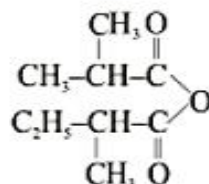
Acetic propionic anhydride (right)

Propionic Acetic anhydride (wrong)

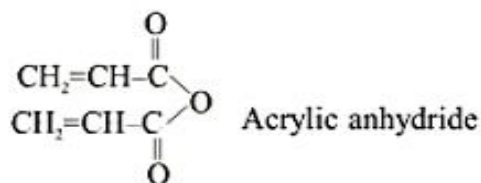
Divide it in two parts as above & name it by suffixing ic anhydride (alphabetically)



Butyric propionic anhydride

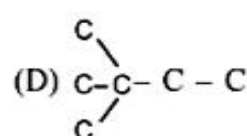
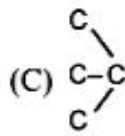
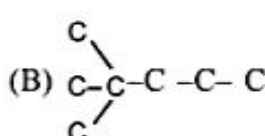
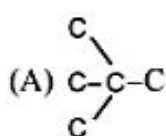


Isobutyric Secondary valeric anhydride



## SOLVED EXAMPLE

**Q.1** Which of the following is not a neo structure:-



**Ans.** C

**Sol.** A carbon must be attached with four carbons.

**Q.2** Acryl aldehyde is -

(A) A saturated aldehyde

(B) An alkene

(C) A polymer

(D) An unsaturated aldehyde

**Ans.** D

**Sol.**  $\text{CH}_2 = \text{CH} - \text{CHO}$  unsaturated aldehyde.

**Q.3** The common name of the compound  $\text{CH}_2 = \text{CH} - \overset{\text{O}}{\parallel}\text{C} - \text{CH} = \text{CH}_2$  is -

(A) Divinyl ketone

(B) Diallyl ketone

(C) Both A and B

(D) None

**Ans.** A

**Sol.**  $\text{CH}_2 = \text{CH} -$  is called as vinyl group.

**Q.4** Common name of  $\text{CH}_2=\text{CH}-\text{CN}$  is :

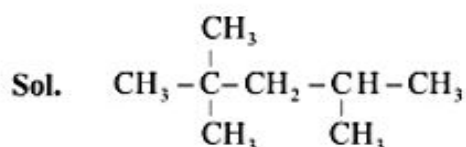
- (a) acrylonitrile      (b) vinyl cyanide      (c) allyl cyanide      (d) allyl nitrile  
 (A) a, b and d      (B) a, and b      (C) only b      (D) a, b and c

**Ans. B**

**Q.5** The number of possible alkyl groups of iso octane are -

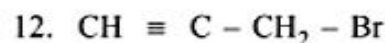
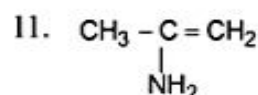
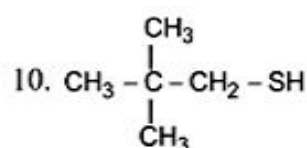
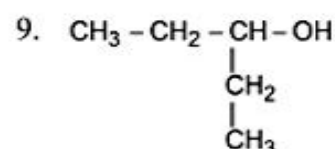
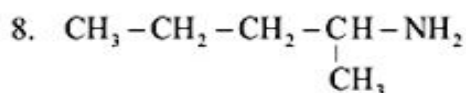
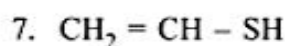
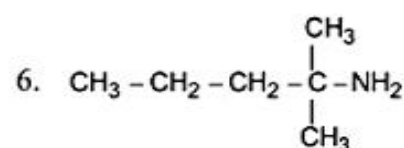
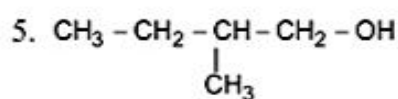
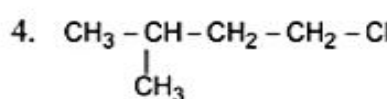
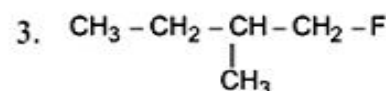
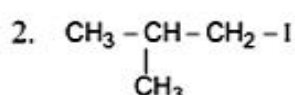
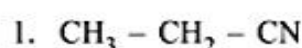
- (A) 1      (B) 3      (C) 5      (D) 6

**Ans. B**



$$1 + 1 + 1 = 3$$

**Q.6** Write the common names of the following compounds



### ANSWERS

1. Ethyl cyanide

3. Active amyl fluoride

5. Active amyl alcohol

7. Vinyl thio alcohol

9. Secondary amyl alcohol.

11. Isopropenyl amine

2. Isobutyl iodide

4. Iso pentyl chloride

6. Tertiary hexyl amine

8. Active secondary amyl amine

10. Neopentyl thio alcohol

12. Propargyl Bromide



---

**MCQ**


---

**Q.1** Which of the following are secondary radicals :

- (a)  $\text{CH}_3 - \overset{|}{\text{CH}} - \text{C}_2\text{H}_5$ , (b)  $\text{CH}_2 = \overset{|}{\text{C}} - \text{CH}_3$ , (c)  $\text{CH}_2 = \text{CH} -$  (d)  $(\text{CH}_3)_2\text{CH} -$   
 (A) a, b, c, (B) a, d, c (C) b, c, d (D) a, b, d

**Q.2** Common name of the structure  $\begin{array}{c} \text{CH}_2 - \text{OH} \\ | \\ \text{CH}_2 - \text{OH} \end{array}$

- (A) Ethylene Glycol (B) Ethene dialcohol (C) Glycerol (D) Ethylene alcohol

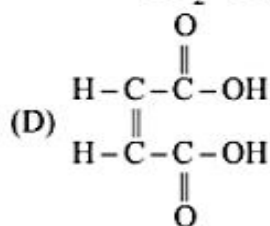
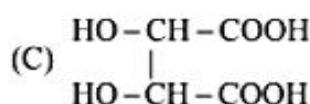
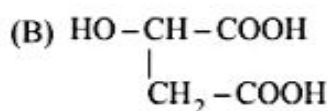
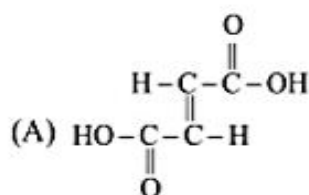
**Q.3** Common name of the compound  $\text{CH}_3 - \text{CH}_2 - \overset{\text{O}}{\parallel} \text{C} - \text{NH}_2$  is -

- (A) Acetamide (B) Propionamide (C) Butyramide (D) Acetic amide

**Q.4** The structure of 2-butenyl radical is :

- (A)  $\text{CH}_3 - \overset{|}{\text{CH}} - \text{C}_2\text{H}_5$  (B)  $\text{CH}_3 - \text{CH} = \text{CH} - \text{CH}_2 -$   
 (C)  $\text{CH}_3 - \text{CH}_2 - \overset{|}{\text{C}} - \text{CH}_3$  (D)  $\text{CH}_2 = \text{CH}_2 - \overset{|}{\text{C}} - \text{CH}_3$

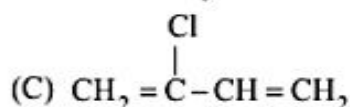
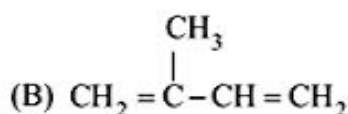
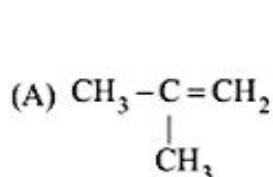
**Q.5** Which one is structure of Maleic acid



**Q.6** Common name of the structure  $\text{CH}_3 - \overset{\text{O}}{\parallel} \text{C} - \text{O} - \text{CH} = \text{CH}_2$  is :

- (A) vinyl acetate (B) acryle acetate (C) methyl acrylate (D) Vinyl ethanoate

**Q.7** Which is the structural formula of isoprene



**Q.8** The number of gem dihalides possible with the molecular formula  $C_2H_4X_2$  and  $C_3H_6X_2$  is given by the set :

- (A) 1, 2                      (B) 2, 1                      (C) 2, 2                      (D) 1, 1

**Q.9** Common name of the compound  $C_6H_5CHO$

- (A) Anisole                      (B) Benzaldehyde                      (C) Salicylaldehyde                      (D) None of these

### ANSWERS

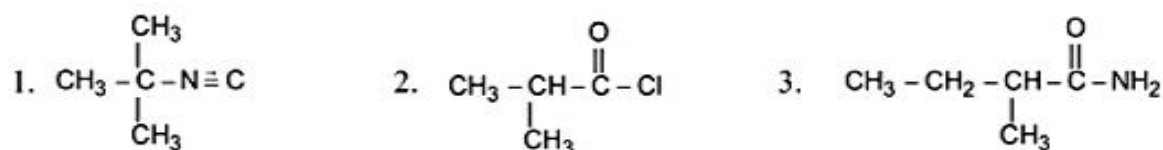
Q.1(D)    Q.2(A)    Q.3(B)    Q.4(B)    Q.5(D)    Q.6(A)    Q.7(B)    Q.8(A)    Q.9(B)

### PROBLEMS

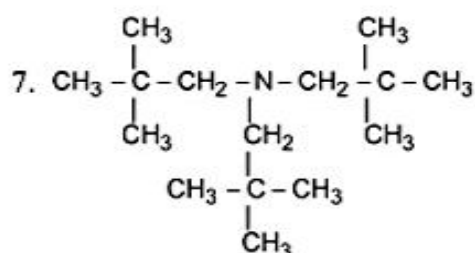
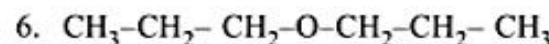
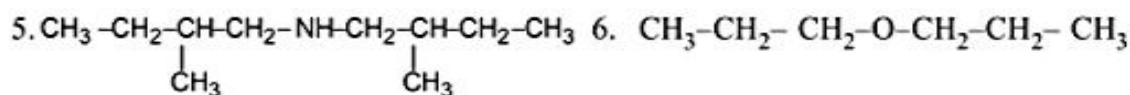
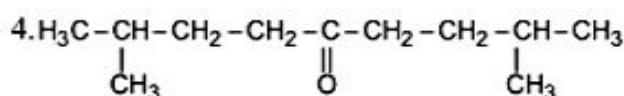
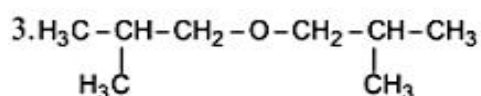
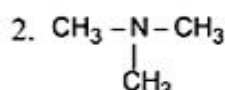
**Q.1** Write down the structures of the following -

- |                         |                           |
|-------------------------|---------------------------|
| 1. Di allyl amine       | 2. Tri methyl amine       |
| 3. Di isobutyl ether    | 4. Di isopentyl ketone    |
| 5. Di Active amyl amine | 6. Di normal propyl ether |
| 7. Tri neopentyl amine  |                           |

**Q.2** Write down the common names of the following :



Ans.(1) 1.  $\text{CH}_2=\text{CH}-\text{CH}_2-\text{NH}-\text{CH}_2-\text{CH}=\text{CH}_2$



Ans. (2) 1. Tertiary valero-isonitrile    2. Isobutyryl chloride    3. Secondary Valer amide

## DERIVED SYSTEM

According to this system name to any compound is given according to the parent name of the homologous series. This system is reserved for the following nine homologous series.

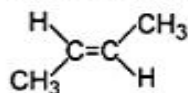
S.No.	Name of Homologous series	Derived Name	Structure of group
1.	Alkane	Methane	$\begin{array}{c}   \\ -\text{C}- \\   \end{array}$
2.	Alkene	Ethylene	$>\text{C}=\text{C}<$
3.	Alkyne	Acetylene	$-\text{C}\equiv\text{C}-$
4.	Alkanol	Carbinol	$\begin{array}{c}   \\ -\text{C}-\text{OH} \\   \end{array}$
5.	Alkanal	Acetaldehyde	$\begin{array}{c}   \\ -\text{C}-\text{CHO} \\   \end{array}$
6.	Alkanoic acid	Acetic acid	$\begin{array}{c}   \\ -\text{C}-\text{COOH} \\   \end{array}$
7.	Alkanoyl halide	Acetyl halide	$\begin{array}{c}   \\ -\text{C}-\text{COX} \\   \end{array}$
8.	Alkanamide	Acetamide	$\begin{array}{c}   \\ -\text{C}-\text{CONH}_2 \\   \end{array}$
9.	Alkanone	Acetone	$\begin{array}{c}   \quad   \\ -\text{C}-\text{C}-\text{C}- \\   \quad    \quad   \\ \quad \text{O} \end{array}$

### Types of Ethylene:– (Symmetrical & Unsymmetrical)

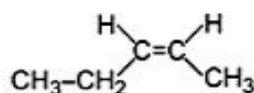
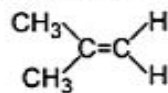
- (a) **Symmetrical** : –In the given two alkyl groups one group is attached to the one carbon of ethylene & next on the next carbon.
- (b) **Unsymmetrical** : – When both the given groups are attached on the same carbon.

**Note : Symmetrical & Unsymmetrical** : –Terms are used only when two alkyl groups are given.  
eg.

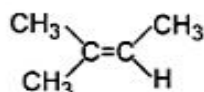
Symmetrical dimethyl ethylene



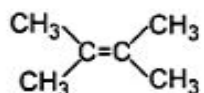
Unsymmetrical dimethyl ethylene



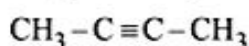
Symmetrical ethyl methyl ethylene



Tri methyl ethylene



Tetra methyl ethylene



Dimethyl acetylene

### PROBLEMS

Write down the derived names of the following compounds

- |   |  |
|---|--|
| <p>1. <math>\text{CH}_2 = \text{CH} - \text{CH}_2 - \text{C} \equiv \text{C} - \text{H}</math></p>  | <p>2. <math display="block">\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3 - \text{C} - \text{OH} \\   \\ \text{CH}_3 \end{array}</math></p>   |
| <p>3. <math display="block">\begin{array}{c} \text{H} \\   \\ \text{CH}_3 - \text{CH}_2 - \text{C} - \text{OH} \\   \\ \text{CH}_3 \end{array}</math></p>                                   | <p>4. <math display="block">\begin{array}{c} \text{CH}_3 \quad \text{O} \\   \quad    \\ \text{CH}_3 - \text{C} - \text{C} - \text{H} \\   \\ \text{CH}_3 \end{array}</math></p>                                       |
| <p>5. <math display="block">\begin{array}{c} \text{H} \quad \text{O} \\   \quad    \\ \text{CH}_3 - \text{CH}_2 - \text{C} - \text{C} - \text{H} \\   \\ \text{CH}_3 \end{array}</math></p> | <p>6. <math display="block">\begin{array}{c} \text{H} \quad \text{O} \\   \quad    \\ \text{CH}_3 - \text{C} - \text{C} - \text{OH} \\   \\ \text{CH}_3 \end{array}</math></p>   |
| <p>7. <math display="block">\begin{array}{c} \text{H} \\   \\ \text{CH}_3 - \text{C} - \text{CH}_3 \\   \\ \text{CH}_3 \end{array}</math></p>   | <p>8. <math display="block">\begin{array}{c} \text{H} \\   \\ \text{CH}_3 - \text{CH}_2 - \text{C} - \text{CH}_3 \\   \\ \text{CH}_3 \end{array}</math></p>  |
| <p>9. <math display="block">\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3 - \text{C} - \text{CH}_3 \\   \\ \text{CH}_3 \end{array}</math></p>  | <p>10. <math display="block">\begin{array}{c} \text{CH}_3 \quad \text{H} \\   \quad   \\ \text{CH}_3 - \text{C} - \text{C} - \text{CH} - \text{CH}_3 \\   \quad   \\ \text{CH}_3 \quad \text{H} \end{array}</math></p> |

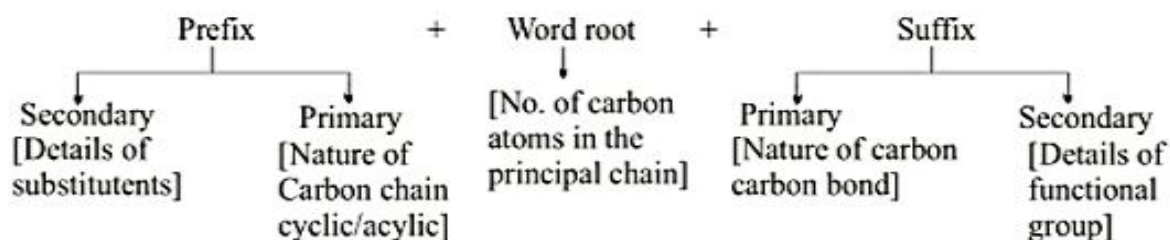
### ANSWERS

- |                                     |  |
|-------------------------------------|--|
| <p>1. Allyl acetylene</p>           | <p>2. Tri methyl carbinol</p>                |
| <p>3. Ethyl methyl carbinol</p>     | <p>4. Tri methyl acetaldehyde</p>            |
| <p>5. Ethyl methyl acetaldehyde</p> | <p>6. Di methyl acetic acid</p>              |
| <p>7. Tri methyl methane</p>        | <p>8. Ethyl di methyl methane</p>            |
| <p>9. Tetra methyl methane</p>      | <p>10. Tertiary butyl Isopropyl methane.</p> |



## IUPAC NOMENCLATURE

The name consists of three parts:



**Primary Prefix :** It represents the nature of the principal / parent chain.

Nature of chain	Primary Prefix
Acyclic / Non-cyclic	—
Cyclic	Cyclo
Bicyclic	Bicyclo
Tricyclic	Tricyclo
Spiro	Spiro

**Secondary prefix :** It represent substituents.

**Word root :** It represents the number of carbon atoms in the principal / parent chain.

No. of carbon atoms	Word root
1	Meth
2	Eth
3	Prop
4	But
5	Pent
6	Hex
7	Hept
8	Oct
9	Non
10	Dec
11	Undec
12	Dodec
13	Tridec
20	Eicos
30	Triacont
40	Tetracont

**Primary Suffix :** It represents the nature of C–C bonds in the principal/ parent chain (whether single bond, double bond or triple bond).

Nature of bond	Primary suffix
<u>Saturated</u> C–C single bond	ane




Nature of bond	Primary suffix
<u>Unsaturated</u>	
C = C bond	ene
C $\equiv$ C bond	yne
2C = C bonds	diene
2C $\equiv$ C bonds	diyne
C = C + C $\equiv$ C	ene + yne = <u>enyne</u>

\* If secondary suffix starts from a vowel or y then the last 'e' of first suffix is omitted.  
**Secondary suffix** : is used for functional groups.

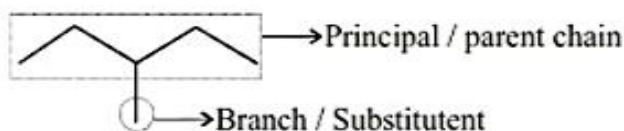
## SATURATED UNBRANCHED HYDROCARBONS

IUPAC name = Word Root + Primary Suffix

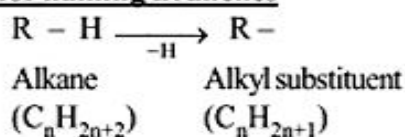
e.g.

CH <sub>4</sub>	Meth + ane	=	Methane
CH <sub>3</sub> - CH <sub>3</sub>	Eth + ane	=	Ethane
CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>3</sub>	Prop + ane	=	Propane
	But + ane	=	Butane
	Pent + ane	=	Pentane
	Hex + ane	=	Hexane
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>9</sub> CH <sub>3</sub>	Undec + ane	=	Undecane
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>28</sub> CH <sub>3</sub>	Triacont + ane	=	Triacontane

## SATURATED BRANCHED CHAIN HYDROCARBONS



### Rules for naming Branches



e.g.

	<u>Alkane</u>	<u>Alkyl</u>	<u>IUPAC names</u>
(1)	CH <sub>4</sub>	-CH <sub>3</sub>	Methyl
(2)	C <sub>2</sub> H <sub>6</sub>	-C <sub>2</sub> H <sub>5</sub>	Ethyl

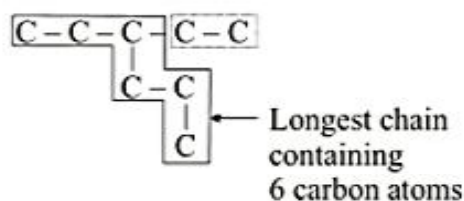
**Naming of complex alkyl groups**

- (i) Longest chain in a branch is selected starting from the same and where it originates from.  
 (ii) Numbering is started from the originating end of a branch.

(3)	$C_3H_8$	$-CH_2CH_2CH_3$	Propyl
		$  \begin{array}{c}  CH_3 \\    \\  -CH \\    \\  CH_3  \end{array}  $	1-Methyl ethyl
(4)	$C_4H_{10}$	$-C_4H_9$	
		$  \begin{array}{ccccccc}  & 4 & 3 & 2 & 1 \\  CH_3 & -CH_2 & -CH_2 & -CH_2 & -CH_2-  \end{array}  $	Butyl
		$  \begin{array}{ccccccc}  & 1 & 2 & 3 \\  CH_3 & -CH & -CH_2 & -CH_3 \\  &   & & \\  & & &   \end{array}  $	1-methyl propyl
		$  \begin{array}{ccccccc}  & & CH_3 & & & & \\  & &   & & & & \\  H_3C & -C^3 & -CH^2 & -CH^1 & -CH_2-  \end{array}  $	2-methyl propyl
		$  \begin{array}{ccccccc}  & & 2CH_3 & & & & \\  & &   & & & & \\  H_3C & -C^1 & -CH_3  \end{array}  $	1,1-dimethylpropyl
(5)		$  \begin{array}{ccccccc}  & & & CH_3 & & & \\  & & &   & & & \\  5CH_3 & -4CH & -3C & -2CH_2 & -1CH_2- \\  &   &   & & \\  & CH_3 & CH_3 & &   \end{array}  $	3,3,4-trimethyl-pentyl

**SATURATED BRANCHED CHAIN HYDROCARBONS****Rules**

- (1) **Longest chain rule** : Select the longest possible carbon chain as the parent chain or principal carbon chain. All other carbon chains will be considered as side chain or substituents.



- (2) If there is more than one longest chain possible then select the chain which contains maximum number of side chains



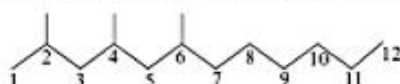
- (3) **Lowest set of locant rule** : The number given to the side chain is locant. While numbering the parent chain, lowest set of locants rule needs to be followed. According to this rule, that set of locants will be considered which has got a lower number at the first point of difference.

I = ( 2, 2, 3, 6, 8) ← Correct

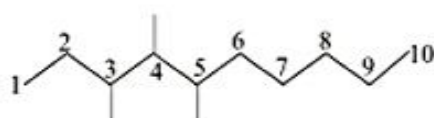
II = ( 2, 2, 4, 4, 5) ← Incorrect

↑  
First point of  
difference

- \* **First set will be considered in this case.**

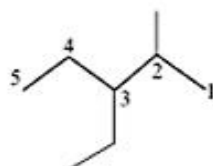


2,4,6-Trimethyldecane (*Correct*)



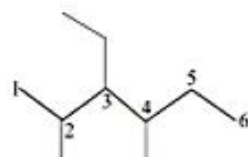
3,4,5-Trimethyldecane (*correct*)

- (a) Side chains are always written in alphabetical order.



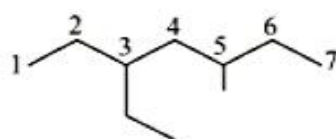
3-Ethyl-2-methylpentane

- (b) Di, tri, tetra etc. are not considered in comparing alphabetical order.

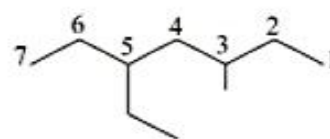


3-Ethyl-2,4-dimethyl hexane

- (c) If lowest set of locants rule is not applicable then numbering is done according to alphabetical order.

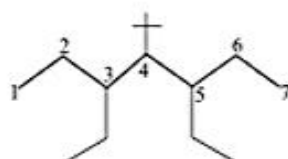


Locant-3, 5 (correct)



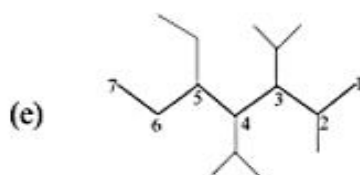
Locant-3, 5 (incorrect)

- (d) If Di, tri, tetra etc. are part of name of complex name then they considered in alphabetical order.



4-(1,1-Dimethyl)-3,5-diethylheptane

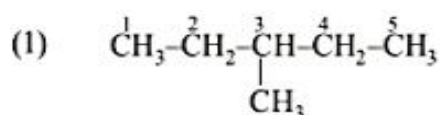




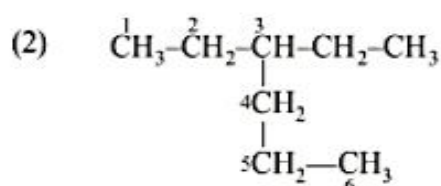
5-Ethyl-3,4-bis(1-methylethyl)-2-methylheptane

bis, tris, tetrakis are used for complex alkyl substituents

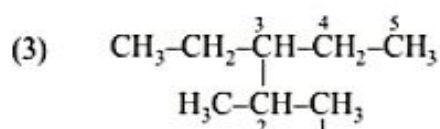
e.g.



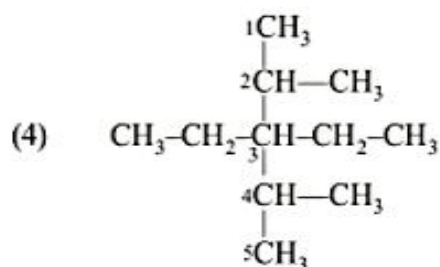
3-methylpentane



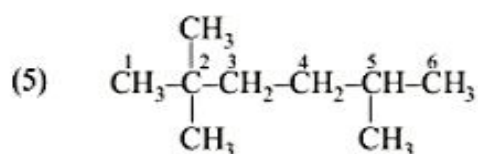
3-ethylhexane



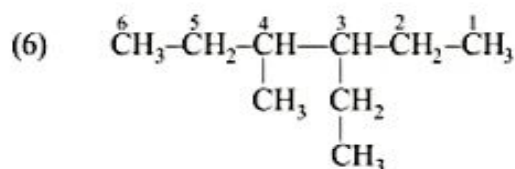
3-ethyl-2-methylpentane



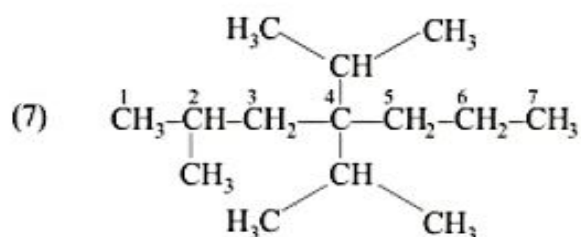
3,3-diethyl-2,4-dimethyl-pentane



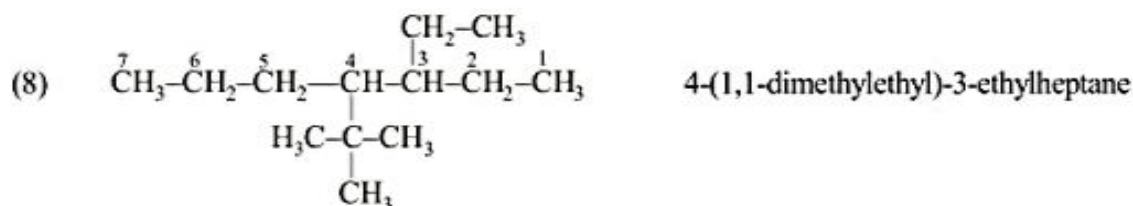
2,2,5-trimethylhexane



3-Ethyl-4-methylhexane



2-methyl-4-bis(1-methylethyl)heptane



### PROBLEMS

Give IUPAC Name of following compounds :

- (1) 
$$\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3\text{CH}_2-\text{C}-\text{CH}_2\text{CH}_3 \\ | \\ \text{CH}_3 \end{array}$$
- (2) 
$$\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3-\text{C}-\text{CH}-\text{CH}_2\text{CH}_3 \\ | \quad | \\ \text{CH}_3 \quad \text{CH}_2\text{CH}_3 \end{array}$$
- (3) 
$$\begin{array}{c} \text{CH}_3-\text{CH}-\text{CH}-\text{CH}_3 \\ | \quad | \\ \text{C}_2\text{H}_5 \quad \text{C}_2\text{H}_5 \end{array}$$
- (4) 
$$\begin{array}{c} (\text{CH}_3\text{CH}_2\text{CH}_2)_2\text{CH}-\text{CH}_2\text{CH}_2\text{CH}_3 \\ | \\ \text{CH} \\ / \quad \backslash \\ \text{H}_3\text{C} \quad \text{CH}_3 \end{array}$$
- (5) 
$$\begin{array}{c} \text{CH}_3-\text{CH}-\text{CH}_2-\text{CH}_3 \\ | \\ \text{H}_3\text{C}-\text{CH}-\text{CH}-\text{CH}_2-\text{CH}_3 \\ | \\ \text{H}_3\text{C}-\text{CH}-\text{CH}_3 \end{array}$$
- (6) 
$$\begin{array}{c} \text{C}_2\text{H}_5 \quad \text{CH}_3 \quad \text{CH}_3 \\ | \quad | \quad | \\ \text{CH}_3\text{CH}_2-\text{CH}-\text{C}-\text{CH}_2-\text{CH}_2-\text{CH}-\text{CH}_2\text{CH}_2\text{CH}_3 \\ | \\ \text{C}(\text{CH}_3)_3 \end{array}$$
- (7) 
$$\begin{array}{c} (\text{CH}_3\text{CH}_2\text{CH}_2)_2\text{CH}-\text{CH}-\text{CH}_2\text{CH}_2\text{CH}_3 \\ | \\ \text{CH}(\text{CH}_3)_2 \end{array}$$
- (8) 
$$\begin{array}{c} \text{CH}_3 \\ | \\ \text{H}_3\text{C}-\text{CH}-\text{CH}-\text{CH}_2\text{CH}_2\text{CH}_3 \\ | \\ \text{CH}_3-(\text{CH}_2)_5-\text{CH}-\text{CH}_2-\text{CH}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \\ | \\ \text{CH}_2\text{CH}_3 \end{array}$$

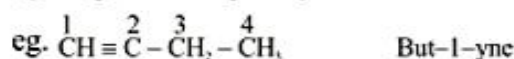
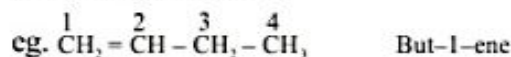
### ANSWERS

- |                                      |  |
|--------------------------------------|--|
| (1) 3,3-Dimethylpentane              | (2) 3-Ethyl-2,2-dimethylpentane                      |
| (3) 3,4-Dimethylhexane               | (4) 4-(1-methylethyl)-4-Propyl heptane               |
| (5) 3-Ethyl-2,4,5-trimethylheptane   | (6) 4-(1,1-Dimethylethyl)-3-ethyl-4,7-dimethylhexane |
| (7) 4-(1-Methylethyl)-5-propyloctane | (8) 7-(1,2-Dimethylpentyl)-5-ethyl tridecane         |

## UNBRANCHED UNSATURATED HYDROCARBON

### Numbering of carbon chain

**Rule-1 :** If unsaturated bond is present in the molecule at the terminal carbon, then numbering done from the side of unsaturated carbon.

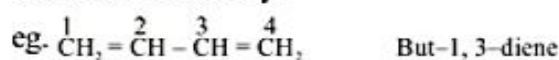


**Rule-2 :** If unsaturated bonds like double bond and triple bond is present at terminal carbon, then numbering always done from double bonded terminal carbon.

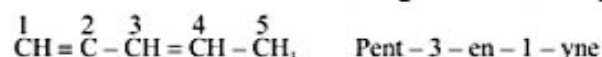
(Double bond preferred over triple bond when both bonds are at same position)



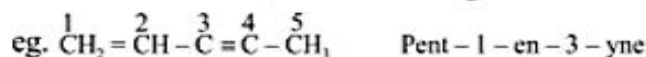
**Rule-3 :** If unsaturated bonds like double bond or triple bond is present at terminal carbon, then numbering is done from either way.




**Rule-4 :** If triple bond is present at terminal carbon and double bond is located at any carbon except other terminal carbon. Then numbering is done from triple bond.



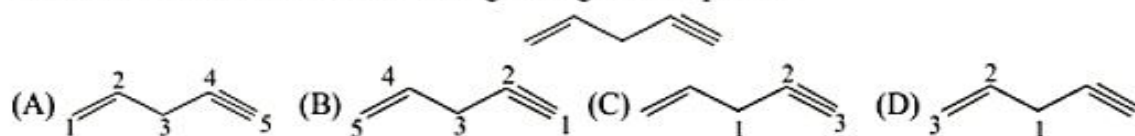
**Rule-5 :** If double bond is present at terminal carbon and triple bond is present at any other position except other terminal carbon, then numbering is done from double bonded terminal carbon.



### MCQ

- Q.1 Correct IUPAC nomenclature of the given compound 
- (A) Hexa-1, 5-dien-3-yne (B) Hex-3-yn-1, 5-diene  
(C) Hex dieneyne (D) Hexeneyne

- Q.2 Which is the correct order for numbering in the given compound.



- Q.3 Write correct IUPAC name for given compound.



- (A) Hexa-2, 4-diyne (B) But-2, 4-diyne (C) Pent-2, 4-diyne (D) Tetra-2, 4-diyne

- Q.4 Which is correct structure for penta-1, 4-diyne



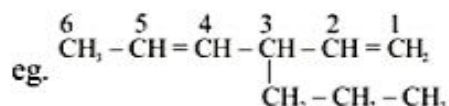
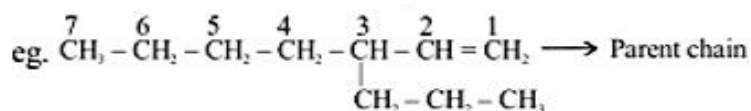
### ANSWERS

- Q.1 (A) Q.2 (A) Q.3 (A) Q.4 (A)

## BRANCHED UNSATURATED HYDROCARBON

### Longest chain :

**Rule-1 :** If unsaturated bonds like double bond or triple bond is present in the molecule, then that parent chain is considered which is containing unsaturated bonds like double bond or triple bond.



**Rule-2 :** A primary suffix is added to the word root to indicate presence at double or triple bond in the parent chain.

For one double bond = Word root + locant + ene

For one triple bond = Word root + locant + yne

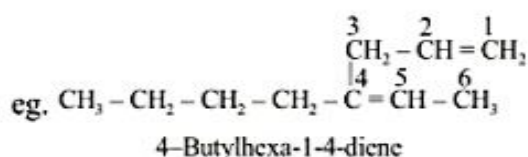
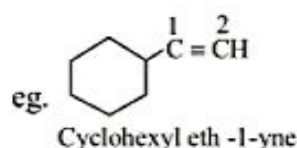
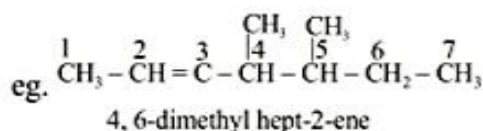
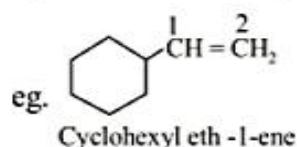
In case the parent chain contains two or more double bonds, the prefixes di, tri, tetra, etc. are used before primary suffix.

For two double bonds = Word root + locant + diene

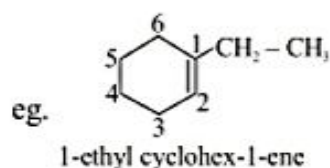
For two triple bonds = Word root + locant + diyne

### Numbering of carbon chain :

**Rule-1 :** In branched alkene, select that parent chain which is containing maximum unsaturated double bond or triple bond and follow properly of lowest locant rule.



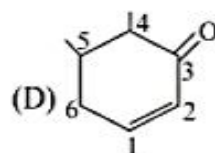
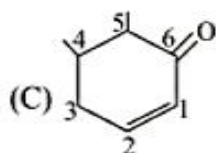
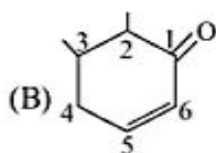
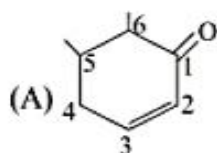
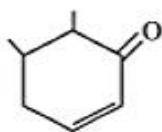
**Rule-2 :** In branched alkene, if unsaturated double bond or triple bond is present in the cyclic ring, then numbering is done from double bonded carbon of the cyclic ring and follow lowest locant rule properly.





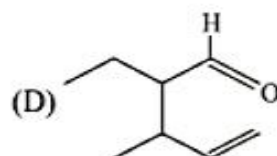
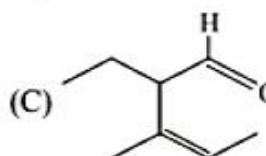
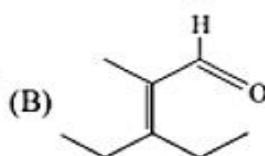
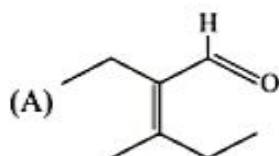
# MCQ

**Q.1** Which is the correct way of number in the given compound.



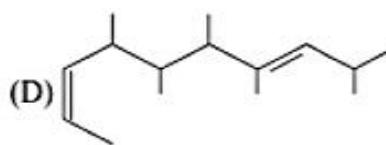
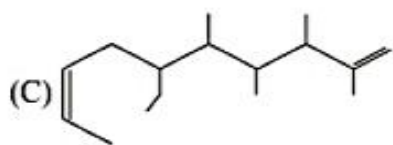
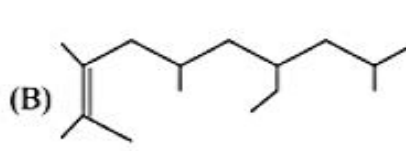
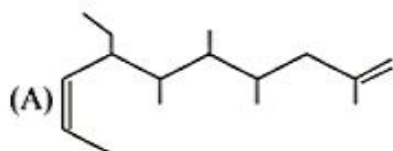
**Q.2** Which is the correct structure for given IUPAC name

2-Ethyl-3-methyl Pent-2-en-1-al



**Q.3** Which is the correct structure for given IUPAC name.

7-ethyl-2, 4, 5, 6-tetramethyl deca-1,8-diene



**Q.4** The IUPAC name of is

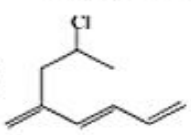
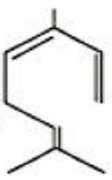
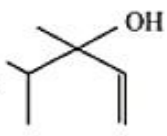
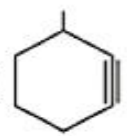
(A) 3-methyl cyclohexene

(B) 1-methyl cyclohex-2-ene


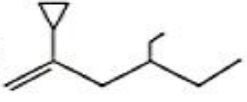
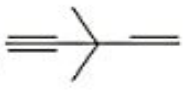
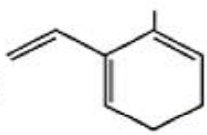
(C) 6-methyl cyclohexene

(D) 1-methyl cyclohex-5-ene

**Q.5** Which is correct match.

IUPAC Name	Structure
(A) 	2-(2'-chloropropyl) hexa-1,3,5-triene
(B) 	3,7-dimethyl hepta-1,3-6-triene
(C) 	3,4-dimethyl pent-1-en-2-ol
(D) 	3-methyl cyclopent-1-yne

**Q.6** Which is incorrect match in the following-

Structure	IUPAC NAME
(A) 	Octa -1- en-4-yne
(B) 	4-Ethyl -2-Cyclopropylhex-1-ene
(C) 	3,3-dimethyl pent-1-en-4-yne
(D) 	2-methyl-3-ethenyl cyclohexa-1,3-diene

### ANSWERS

Q.1 (A)    Q.2 (A)    Q.3 (A)    Q.4 (A)    Q.5 (A)    Q.6 (D)

## IUPAC NAMING OF ORGANIC COMPOUND CONTAINING FUNCTIONAL GROUPS

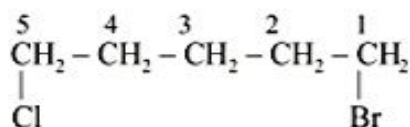
In IUPAC nomenclature functional groups are categorized into two type.

**Type I :** Groups of this type are not considered as functional groups in IUPAC nomenclature. They are considered as substituents & therefore represented by prefix. type I functional group & their prefix are shown below:

Groups	Prefix
- F	fluoro
- Cl	chloro
- Br	bromo
- I	iodo
- NO <sub>2</sub>	nitro
- NO	nitroso
- OR	alkoxy
$\begin{array}{c} \diagup \quad \diagdown \\ \text{C} - \text{C} - \\ \diagdown \quad \diagup \\ \text{O} \end{array}$	epoxy

### Rules for their nomenclature :

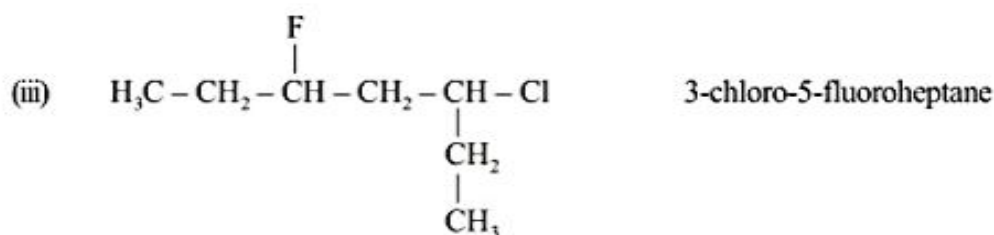
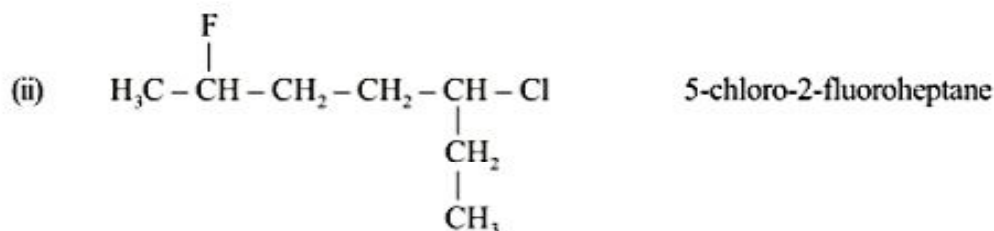
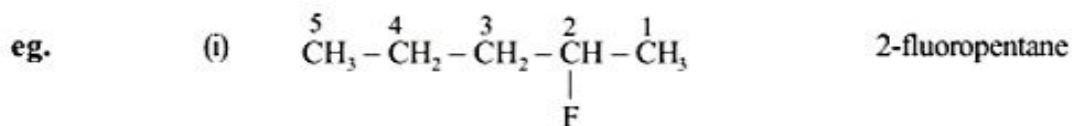
**Rule I :** If two substituents are present on same position from different ends, then priority is decided on the basis of alphabetical order.



**Rule II :** If multiple bond and type I functional group both are present, the priority is given to multiple bond.

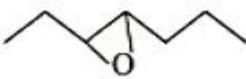
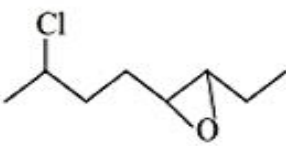

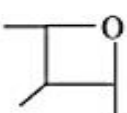


**Rule III :** These groups are written in alphabetical order in IUPAC name.



- (iv)  $\begin{array}{ccccccc} \text{H}_3\text{C} & -\text{CH} & -\text{CH} & -\text{CH} & -\text{CH}_3 \\ & | & | & | \\ & \text{CH}_2 & \text{NO}_2 & \text{CH}_2 \\ & | & & | \\ & \text{CH}_3 & & \text{CH}_3 \end{array}$  3,5-dimethyl-4-nitro heptane
- (v)  $\begin{array}{ccccccc} \text{CH}_2 & -\text{CH}_2 & -\text{CH} & -\text{CH}_2 & -\text{C} & -\text{CH}_2 & -\text{CH}_3 \\ | & & | & & || & & \\ \text{NO} & & \text{I} & & \text{CH}_2 & & \end{array}$  2-ethyl-4-iodo-6-nitroso hex-1-ene
- (vi)  $\begin{array}{ccccccc} \text{HC} & =\text{CH} & -\text{C} & -\text{CH}_2 & -\text{CH}_2 & -\text{Cl} \\ | & & || & & & \\ \text{Cl} & & \text{CH}_2 & & & \end{array}$  1-chloro-3-chloroethylbuta-1,3-diene
- (vii)  $\text{H}_3\text{C} - \text{CH}_2 - \text{O} - \text{CH}_2 - \text{CH}_3$  ethoxy ethane
- (viii)  $\text{H}_3\text{C} - \text{CH}_2 - \text{O} - \text{CH}_2 - \text{CH}_2 - \text{CH}_3$  1-ethoxy propane
- (ix)  $\begin{array}{ccccccc} \text{H}_3\text{C} & -\text{CH}_2 & -\text{CH} & -\text{O} & -\text{CH}_2 & -\text{CH}_2 & -\text{CH}_3 \\ & & | & & & & \\ & & \text{CH}_3 & & & & \end{array}$  2-propoxy butane
- (x)  $\begin{array}{ccccccc} \text{H}_3\text{C} & -\text{CH}_2 & -\text{CH} & -\text{O} & -\text{CH} & -\text{CH}_3 \\ & & | & & | & \\ & & \text{CH}_3 & & \text{CH}_3 & \end{array}$  2-(methyl ethoxy) butane or 2-isopropoxy butane

**Epoxides :**

- (1)  $\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_2 \\ \quad \quad \quad \diagdown \quad \diagup \\ \quad \quad \quad \text{O} \end{array}$  1,2-epoxy propane
- (2)  3,4-epoxy heptane
- (3)  2-chloro-5,6-epoxy octane
- (4)  1,3-epoxy propane
- (5)  2,4-epoxy-3-methyl pentane

**Type-II :** Groups of this type are treated as functional groups and represented by suffix in IUPAC nomenclature.  
Priority table for functional group.



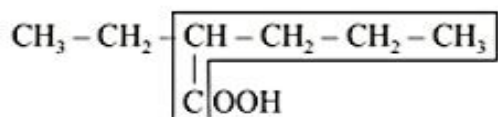
S.No.	Functional group	Name	Suffix	Prefix
(1)	$\begin{array}{c} \text{O} \\    \\ -\text{C}-\text{OH} \end{array}$	Carboxylic acid	oic acid	Carboxy
(2)	$-\text{SO}_3\text{H}$	Sulphonic acid	sulphonic acid	Sulpho
(3)	$\begin{array}{c} -\text{C}-\text{O}-\text{C}- \\    \quad \quad    \\ \text{O} \quad \quad \text{O} \end{array}$	Acid anhydride	oic anhydride	–
(4)	$\begin{array}{c} -\text{C}-\text{OR} \\    \\ \text{O} \end{array}$	Ester	oate (alkyl+w.r.+oate)	Alkoxy carbonyl
(5)	$\begin{array}{c} -\text{C}-\text{Cl} \\    \\ \text{O} \end{array}$	Acid chloride	oyl chloride	Chlorocarbonyl
(6)	$\begin{array}{c} -\text{C}-\text{NH}_2 \\    \\ \text{O} \end{array}$	Amide	amide	Carbamoyl
(7)	$-\text{C} \equiv \text{N}$	Cyanide	nitrile	Cyano
(8)	$-\text{N} \equiv \text{C}$	Isocyanide	isonitrile	Isocyano
(9)	$-\text{CHO}$	Aldehyde	al	oxo / formyl
(10)	$\begin{array}{c} -\text{C}- \\    \\ \text{O} \end{array}$	Ketone	one	Oxo/Keto
(11)	$-\text{OH}$	Alcohol	ol	Hydroxy
(12)	$-\text{SH}$	Thio-alcohol	thiol	Mercapto
(13)	$-\text{NH}_2$	Amine	amine	Amino
(14)	$(=)$		ene	
(15)	$(\equiv)$		yne	

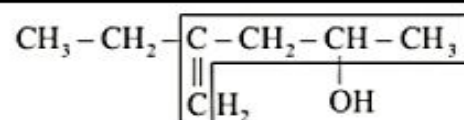
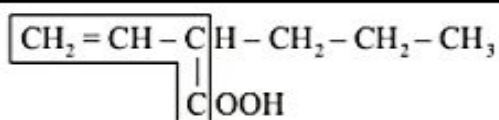
**Note :** Double bond & triple bond are not true functional groups.

w.r. → Word Root

**Rule for their nomenclature :**

- (1) Selection of parent 'C' chain : longest possible 'C' chain with functional group and having maximum number of multiple bonds is selected as parent 'C' chain.





(2) Numbering:

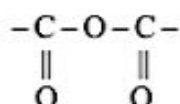
(a) Numbering starts from the side of functional group for numbering priority order is given below :

Functional group > Multiple bonds > Substituents

(b) If chain ending 'C' containing functional group is present then numbering starts from the 'C' of functional group these functional groups are known as DON category functional groups functional groups of this category are shown below :

- COOH

- CN



- CHO

- COOR

- COCl

- CONH<sub>2</sub>

**Rule 3 :** 'e' of primary suffix is dropped if secondary suffix starts from a vowel.

Example of compounds having don category functional groups :

(i)  $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{COOH}$

Butanoic acid

(ii)  $\text{CH}_3 - \text{CH} - \text{CH}_2 - \text{CH}_3$   
 $\quad \quad |$   
 $\quad \quad \text{COOH}$

2-methyl butanoic acid

(iii)  $\text{CH}_3 - \text{CH}_2 - \text{C} - \text{CH}_2 - \text{CH}_2 - \overset{\text{O}}{\parallel} \text{C} - \text{Cl}$   
 $\quad \quad \quad ||$   
 $\quad \quad \quad \text{CH}_2$

4-ethyl pent-4-en-1-oylchloride

(iv)  $\begin{array}{c} \text{O} \\ || \\ \text{H} - \text{C} - \text{NH}_2 \end{array}$

methanamide

(v)  $\begin{array}{c} \text{CHO} \\ | \\ \text{CHO} \end{array}$

ethandial

(vi)  $\text{NC} - \text{CH}_2 - \text{CH}_2 - \text{CH}_3$

butane nitrile

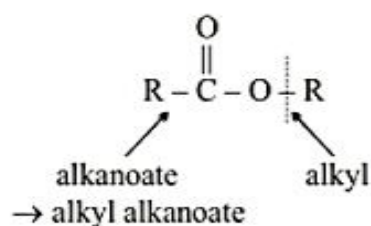
(vii)  $\text{H}_2\text{N} - \overset{\text{O}}{\parallel} \text{C} - \text{CH}_2 - \text{CH} - \text{CH}_2 - \text{CH} = \text{CH}_2$   
 $\quad \quad \quad |$   
 $\quad \quad \quad \text{CH}$   
 $\quad \quad \quad ||$   
 $\quad \quad \quad \text{CH}_2$

3-ethenyl hex-5-en-1-amide

(viii)  $\begin{array}{c} \text{O} \\ || \\ \text{CH}_2 = \text{CH} - \text{CH} - \text{C} - \text{Cl} \\ | \\ \text{Cl} - \text{H}_2\text{C} - \text{H}_2\text{C} - \text{CH}_2 \end{array}$

2-(3-chloropropyl) but-3-en-1-oyl chloride

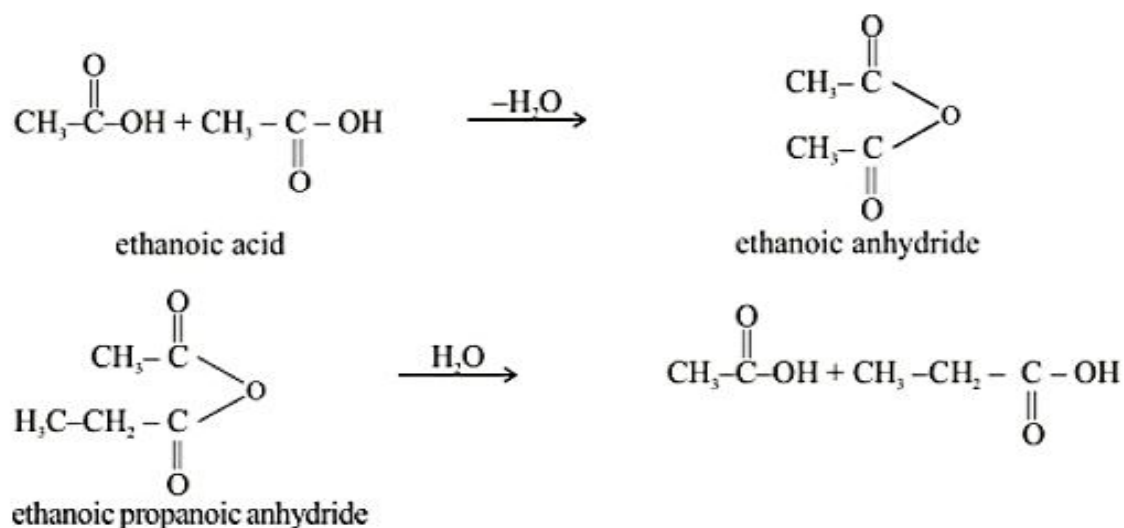
**Ester :**

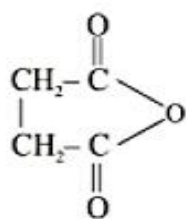


**e.g.**

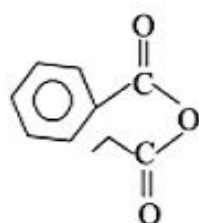
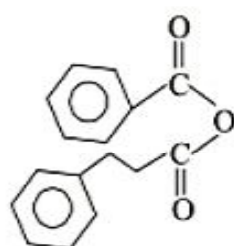
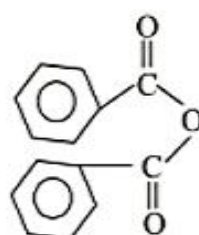
- (i)  $\text{CH}_3 - \overset{\text{O}}{\parallel} \text{C} - \text{O} - \text{CH}_3$  Methyl ethanoate
- (ii)  $\text{H} - \overset{\text{O}}{\parallel} \text{C} - \text{O} - \text{CH}_2 - \text{CH}_3$  ethyl methanoate
- (iii)  $\text{CH}_3 - \underset{\text{CH}_2 - \text{Cl}}{\text{CH}} - \text{CH}_2 - \overset{\text{O}}{\parallel} \text{C} - \text{O} - \text{CH}_3$  methyl-4-chloro-3-methyl butanoate
- (iv)  $\text{Cl} - \text{CH}_2 - \text{O} - \overset{\text{O}}{\parallel} \text{C} - \text{CH}_3$  chloromethylethanoate
- (v)  $\text{H}_3\text{COOCCH}_3$  methyl ethanoate
- (vi)  $\text{H}_3\text{C} - \text{H}_2\text{C} - \underset{\text{O}}{\overset{\text{O}}{\parallel}} \text{CH} - \overset{\text{O}}{\parallel} \text{C} - \text{O} - \text{CH}_3$  methyl-2-ethyl butane-1, 4-dioate.

**Anhydride :** Nomenclature of anhydride is done on the basis of the carboxylic acid from which it is obtained.

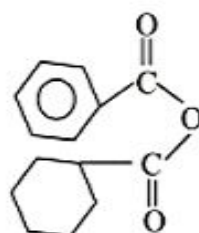




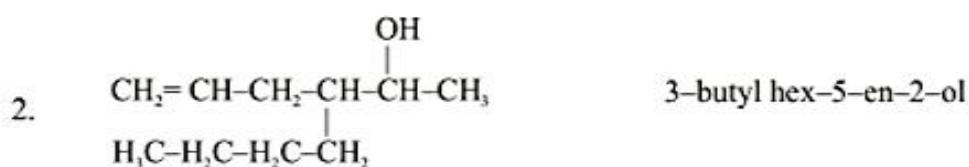
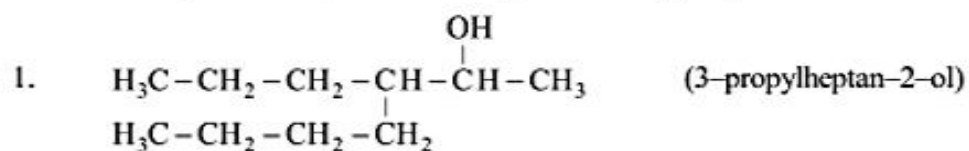
butanedioic anhydride

Benzene carboxylic  
propanoic anhydrideBenzene carboxylic-3-phenyl  
propanoic anhydride

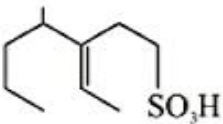
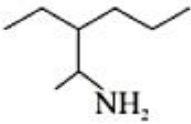
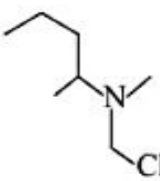
Benzene carboxylic anhydride

Benzene carboxylic cyclohe  
carbocyclic anhydride

**Example of compounds having functional group other than DON category :**





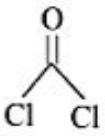
3. 
$$\begin{array}{c} \text{SH} \\ | \\ \text{H}_3\text{C}-\text{C}=\text{C}-\text{CH}_2-\text{CH}_3 \\ || \\ \text{CH}_2 \end{array} \quad \text{2-methylpent-1-ene-3-thiol}$$
4. 
$$\begin{array}{c} \text{Me} \\ | \\ \text{CH}_2-\text{CH}-\text{SO}_3\text{H} \\ | \\ \text{CH}_2-\text{CH}-\text{SO}_3\text{H} \\ | \\ \text{Et} \end{array} \quad \text{heptane-2, 5-disulphonic acid}$$
5. 
$$\text{CH}_3-\text{CH}=\text{CH}-\underset{\text{CH}_2}{\underset{||}{\text{C}}}-\text{CH}_2-\overset{\text{O}}{\overset{||}{\text{C}}}-\text{CH}_2-\text{CH}_3 \quad \text{5-methylene oct-6-en-3-one}$$
6.   $\text{SO}_3\text{H}$  3-(1-methyl butyl) pent-3-ene-1-sulphonic acid
7.  3-ethylhexan-2-amine
8. 
$$\text{CH}_3-\text{CH}_2-\underset{\text{NH}-\text{CH}_2-\text{CH}_3}{\text{CH}}-\text{CH}_2-\text{CH}_3 \quad \text{N-ethyl pentan-3-amine}$$
9.  N-Chloromethyl-N-methyl pentan-2-amine

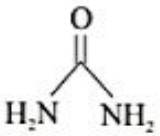
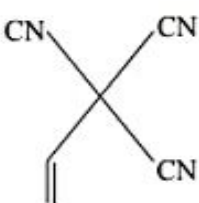
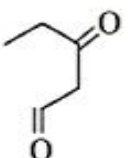
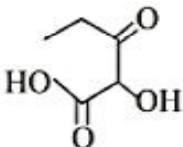
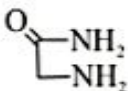
## POLYFUNCTIONAL COMPOUNDS

**Rule-I :** If more than one functional groups are present then one is selected as principal functional group and represented by suffix. Other functional groups are treated as substituents & represented by prefix.

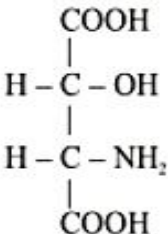
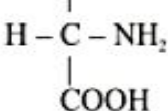
Selection of principal functional group is done according to priority table

1. 
$$\text{HS}-\text{CH}_2-\underset{\text{CH}_3}{\underset{|}{\text{CH}}}-\overset{\text{O}}{\overset{||}{\text{C}}}-\text{OH} \quad \text{(3-mercapto-2-methylpropanoic acid)}$$


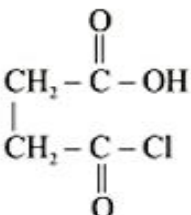
2.  chloromethanoylchloride

3.  amino methanomide (Urea)
4.  2-ethenyl-2-isocyano propane-1,3-dinitrile
5.  3-oxo pentanal
6.  2-hydroxy-3-oxo pentanoic acid
7.  2-amino ethanamide

**Rule-II :** When principal group is selected then there is no use of priority table.

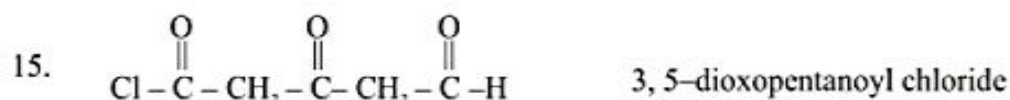
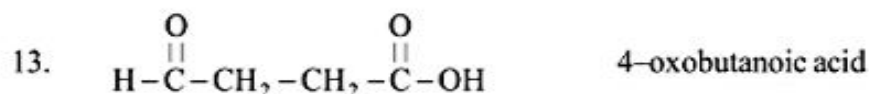
8.  3-amino-2-hydroxy butane - 1, 4-dioic acid (Incorrect)
8.  2 - amino - 3 - hydroxybutane -1, 4-dioic acid (Correct)

**Rule-III :** If any DON functional group is present as sec. functional group then its 'c' is not included in principal 'c' chain except -CHO group.

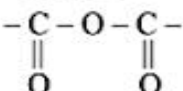
9.  3-cyanopropanoic acid
10.  3-Chloro carbonylpropanoic acid



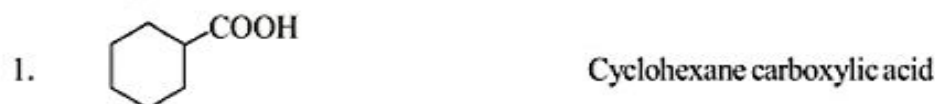
**Rule-IV :** As secondary functional group, if 'C' of -CHO group is included in parent 'c' chain then oxo is used as prefix, otherwise we use formyl group as prefix.

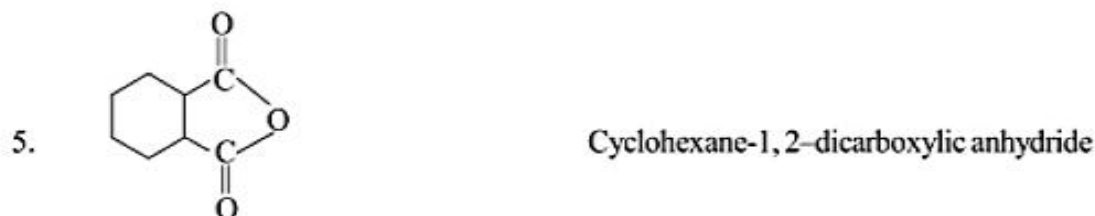
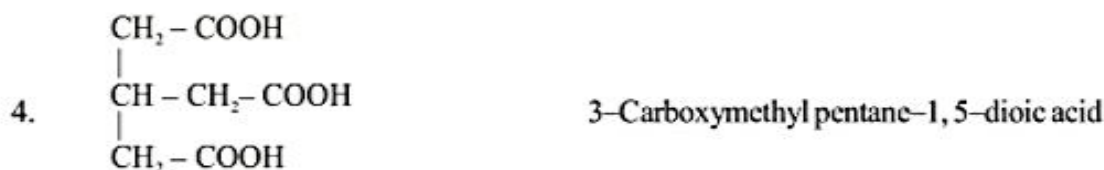


**IUPAC nomenclature if DON category functional group is present as principal functional group & its 'c' is not included in parent 'c' chain →**

- COOH	Carboxylic acid
	Carboxylic anhydride
- COOR	Carboxylate
- COCl	Carbonyl chloride
- CONH <sub>2</sub>	Carboxamide
- CN	Carbonitrile
- CHO	Carbaldehyde

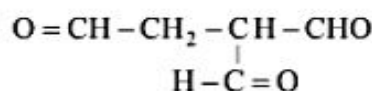
e.g.





### SOLVED EXAMPLES

**Q.1** The correct IUPAC name of the following compound is



(A) 1,1-diformyl propanal

(B) 3-formyl butanedial

(C) 2-formyl butanedial

(D) 1,1,2-ethane tricarbaldehyde

**Ans.** D

**Sol.** The principal functional group is  $-\text{CHO}$ . 
$$\text{O} = \text{CH} - \overset{2}{\text{CH}_2} - \overset{1}{\underset{\text{CHO}}{\text{CH}}} - \text{CHO}$$
 1,1,2-Ethanetricarbaldehyde

**Q.2** The correct IUPAC name of compound  $\text{CH}_3 - \text{CH}_2 - \underset{\text{O}}{\underset{||}{\text{C}}} - \underset{\text{CN}}{\underset{|}{\text{CH}}} - \text{CHO}$  is :

(A) 2-cyano-3-oxopentanal

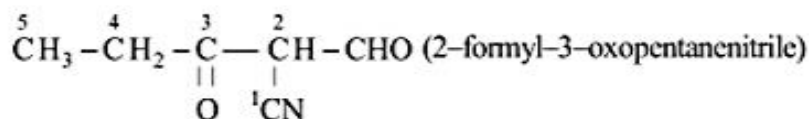
(B) 2-formyl-3-oxopentanenitrile

(C) 2-cyano-1,3-pentanedione

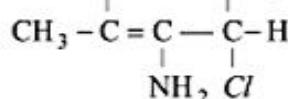
(D) 1,3-dioxo-2-cyanopentane

**Ans.** B

**Sol.** Here the main functional group is  $-\text{CN}$ , which had nitrile suffix and  $\text{CHO}$  and  $\text{CO}$  are taken as substituents.



**Q.3** The IUPAC name of compound  $\text{HO} - \underset{\text{CH}_3}{\underset{|}{\text{C}}} = \underset{\text{NH}_2}{\underset{|}{\text{C}}} - \underset{\text{Cl}}{\underset{|}{\text{C}}} - \text{CH}_3$  is



(A) 2-amino-3-chloro-2-methyl-2-pentenoic acid

(B) 3-amino-4-chloro-2-methyl-2-pentenoic acid

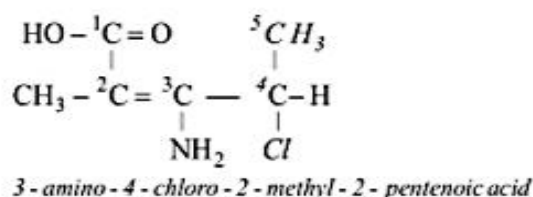
(C) 4-amino-3-chloro-2-methyl-2-pentenoic acid

(D) none of these

**Ans.** B



**Sol.** The principal functional group is carboxylic acid ( $-\text{COOH}$ )



- Q.4** IUPAC name of compound  $\text{CH}_3\text{CH}_2\text{O}\overset{\text{O}}{\parallel}\text{CCH}_2\text{CH}_2\text{CH}_3$  is  
 (A) Propyl propanoate (B) Ethyl butanoate  
 (C) Propyl butanoate (D) Ethyl propanoate

**Ans.** B

**Sol.**  $\text{CH}_3-\text{CH}_2-\text{O}-\overset{1}{\text{C}}-\overset{2}{\text{CH}_2}-\overset{3}{\text{CH}_2}-\overset{4}{\text{CH}_3}$

### MCQ

- Q.1** The IUPAC name of the compound having structure  $\text{ClCH}_2-\text{CH}_2-\text{COOH}$  is :  
 (A) 3-Chloro propanoic acid (B) 2-Chloro propanoic acid  
 (C) 2-Chloro ethanoic acid (D) Chloro succinic acid

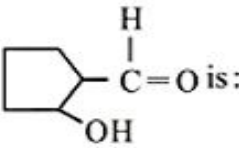
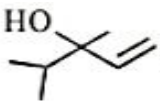
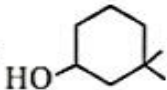
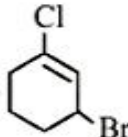
- Q.2** The IUPAC Name of compound  $\text{CH}_3-\overset{\text{OH}}{\underset{\text{CH}_3}{\text{C}}}-\text{CH}_2-\text{OH}$  is :  
 (A) 2-Methyl-1, 2-propanediol (B) Isobutylene glycol  
 (C) 1-2-Dihydroxy-2-Methyl propane (D) 2-Hydroxy methyl-2-propanol

- Q.3** The IUPAC name of  $\text{CH}_3-\overset{\text{CH}_3}{\underset{\text{O}}{\parallel}}\text{CH}-\text{C}-\text{CH}_2-\text{CH}_2\text{OH}$  is -  
 (A) 1-Hydroxy-4-methyl-3-pentanone (B) 2-Methyl-5-hydroxy-3-pentanone  
 (C) 4-Methyl-3-oxo-1-pentanol (D) Hexanol-1-one-3

- Q.4** IUPAC name of  $\text{CH}_3-\overset{\text{Cl}}{\underset{\text{CH}_3}{\text{CH}}}-\text{CH}-\text{H}_2\text{C}-\text{CH}_2-\text{H}_2\text{C}-\text{CH}_2-\text{Br}$   
 (A) 2-Chloro-3-methyl-7-bromo heptane (B) 7-Bromo-2-chloro-3-methyl heptane  
 (C) 1-Bromo-5-methyl-6-chloro heptane (D) 1-Bromo-6-chloro-5-methyl heptane

- Q.5** IUPAC name of  $\text{CH}_2=\text{CH}-\text{CH}_2-\text{Cl}$  is :  
 (A) Allyl chloride (B) 1-Chloro-3-propene  
 (C) 3-Chloro-1-propene (D) Vinyl chloride



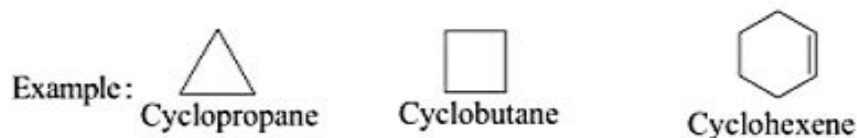
- Q.14 The correct name for  is:
- (A) 2-Hydroxy cyclopentanal (B) 2-Formyl-1-hydroxy cyclopentane  
(C) 2-Hydroxy cyclopentane carbaldehyde (D) Cyclopentane-2-ol-1-al
- Q.15 The IUPAC name of  $\text{Cl}-\text{C}(=\text{O})-\text{OC}_2\text{H}_5$  is:
- (A) Ethoxy formyl chloride (B) Ethoxy methanoyl chloride  
(C) Ethyl chloro methanoate (D) Ethoxy carbonyl chloride
- Q.16 IUPAC name of  $\text{CH}_3-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_2-\underset{\text{CN}}{\text{CH}}-\text{CH}_3$  is:
- (A) 2-cyano-3-methyl hexane (B) 3-methyl-5-cyano hexane  
(C) 2,4-Dimethyl pentanenitrile (D) 2-cyano-3-methylhexane
- Q.17  has the IUPAC name:
- (A) 3,4-Dimethyl-1-penten-3-ol (B) Isopropyl-3-methyl vinyl carbinol  
(C) 2,3-Dimethyl-4-penten-3-ol (D) None of the above
- Q.18 Which of the following compound has wrong IUPAC name?
- (A)  $\text{CH}_3\text{CH}_2-\text{CH}_2\text{COO}-\text{CH}_2\text{CH}_3$   
(Ethyl butanoate)
- (B)  $\text{CH}_3-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_2-\text{CHO}$   
(3-Methylbutanal)
- (C)  $\text{CH}_3-\underset{\text{OH}}{\text{CH}}-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_3$   
(2-Methyl-3-butanol)
- (D)  $\text{CH}_3-\underset{\text{CH}_3}{\text{CH}}-\underset{\text{O}}{\text{C}}-\text{CH}_2-\text{CH}_3$   
(2-Methyl-3-pentanone)
- Q.19 The IUPAC name of the compound  is:
- (A) 1,1-dimethyl-3-cyclohexanol (B) 1,1-dimethyl-3-hydroxy cyclohexane  
(C) 3,3-dimethyl-1-cyclohexanol (D) 3,3-dimethyl-1-hydroxy cyclohexane
- Q.20 The IUPAC name of the compound is 
- (A) 6-bromo-2-chlorocyclohexene (B) 3-bromo-1-chlorocyclohexene  
(C) 1-bromo-3-chlorocyclohexene (D) 2-bromo-6-chlorocyclohex-1-ene

## ANSWERS

Q.1 (A) Q.2 (A) Q.3 (A) Q.4 (D) Q.5 (C) Q.6 (C) Q.7 (B) Q.8 (C) Q.9 (B) Q.10 (A) Q.11 (A)  
Q.12 (D) Q.13 (B) Q.14 (C) Q.15 (C) Q.16 (C) Q.17 (A) Q.18 (C) Q.19 (C) Q.20 (B)

## NOMENCLATURE OF ALICYCLIC COMPOUNDS

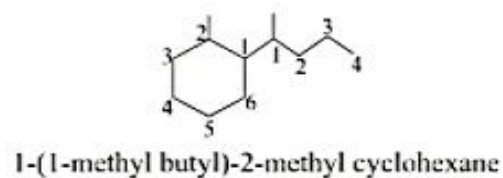
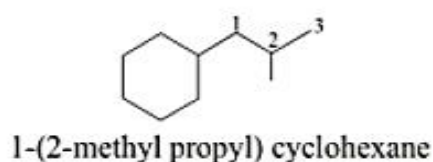
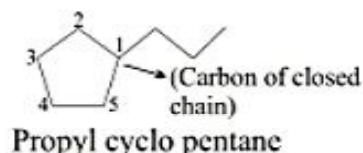
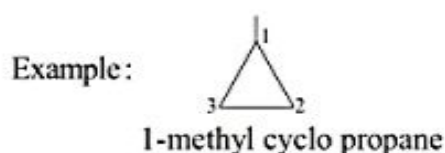
- (A) Unsubstituted cyclo compounds : Prefix + word root + suffix  
Cyclo + no. of C + ane / ene



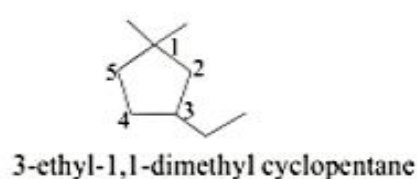
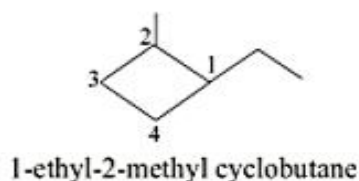
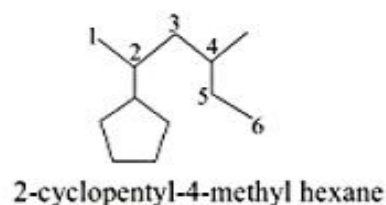
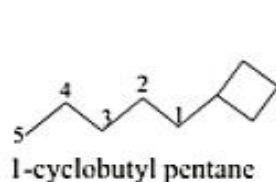
- (B) Substituted cyclic compound (closed + open chain saturated)

**Rule :**

- (i) If number of carbons in closed chain  $\geq$  no. of carbons in open saturated chain, then closed chain will be selected as parent chain.

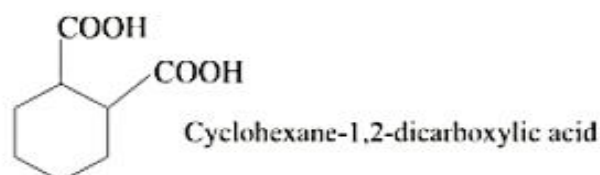
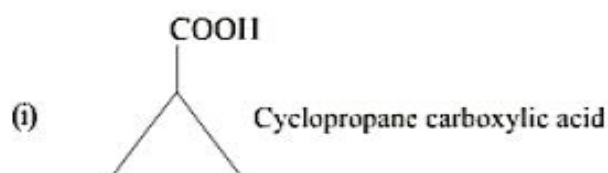


- (ii) If number of carbons in open chain  $>$  closed chain  $\Rightarrow$  Open chain is parent chain

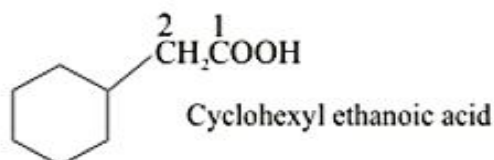


**Rule :**

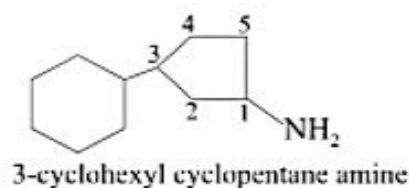
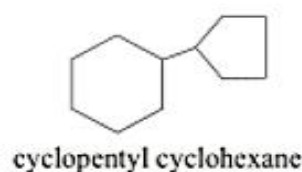
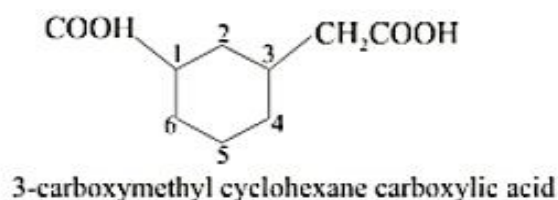
Cyclic compounds with functional group is considered as parent chain :







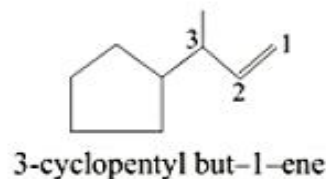
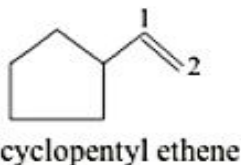
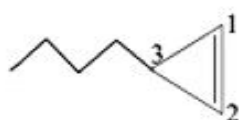
→ If FG ( $-\text{COOH}$ ) present on both cyclic and non-cyclic then number of carbon atoms is considered.



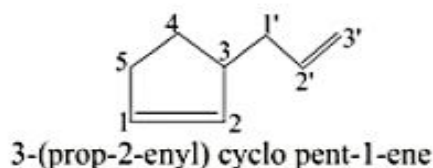
**If unsaturation (Multiple bond) present**

**Rule :**

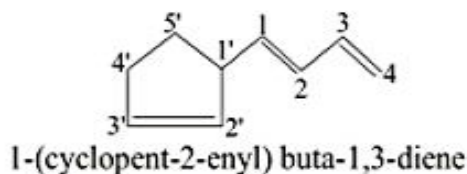
Chain containing multiple bond is selected as parent chain



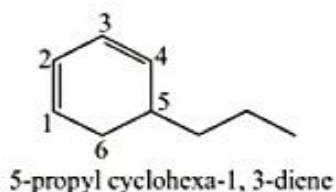
If ring and non-cyclic side chain both containing double bond then check the number of C atoms and given parent chain.

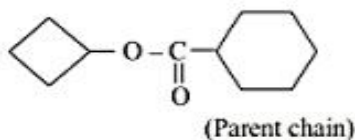


Number of double bond is considered while selecting parent chain

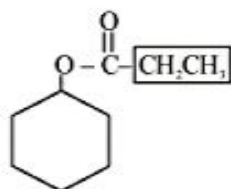


In case of more than one multiple bond use suffix 'a' after word root.

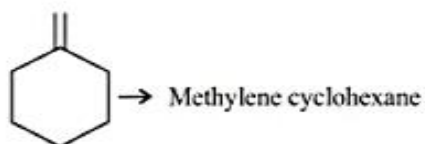
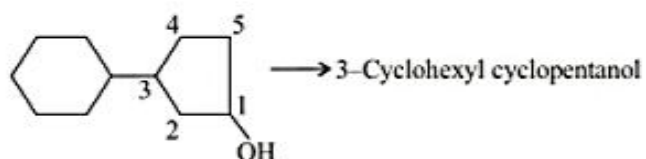
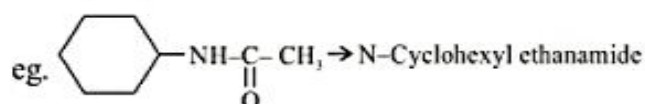
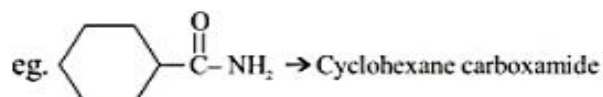
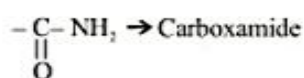




Cyclobutyl cyclohexane carboxylate

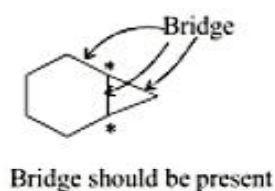
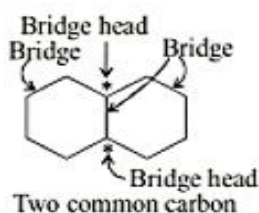


Cyclohexyl ethane carboxylate



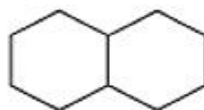
## NOMENCLATURE OF BICYCLO COMPOUNDS

Bicyclo compounds : If two rings are fused at two common carbon atoms then compound are known as bicyclic compound.

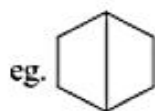


### (i) Unsubstituted bicyclo compounds

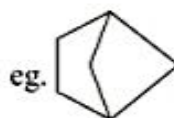
Prefix      +      Numbering of      +      Suffix  
Bicyclo      carbon atoms in  
                         each bridge in  
                         decreasing order



Bicyclo [4.4.0] decane  
(Bridge head C not considered)



Bicyclo [2.2.0] Hexane



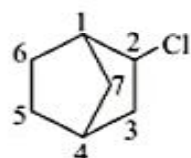
Bicyclo [2,1,1] Hexane



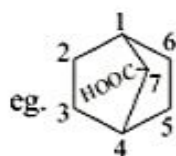
Bicyclo [3,2,0] Heptane

(ii) **Substituted bicyclo (Bicyclo with substitution or functional group)**

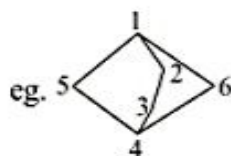
In substituted bicyclic compounds numbering starts from a bridge head carbon atom and proceeds towards longest bridge then smaller bridge & then smallest bridge.



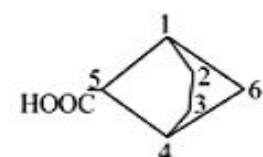
2-Chloro bicyclo [2.2.1] heptane



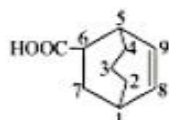
bicyclo [2.2.1] heptane-7-carboxylic acid



Bicyclo [2.1.1] hexane



Bicyclo [2.1.1] hexane-5-carboxylic acid



F.G. is preferred over double bond.  
Bicyclo [3.2.2] dec-9-en-carboxylic acid

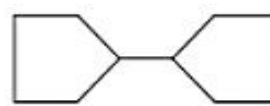
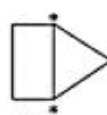
Bicyclo [3.2.2] non-8-ene-6-carboxylic acid

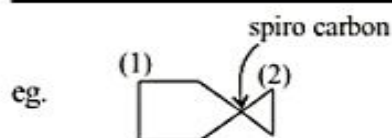
**NOMENCLATURE OF SPIRO COMPOUNDS**

Spiro comp. - Two cyclic rings are fused at one common carbon (only one bridge head)

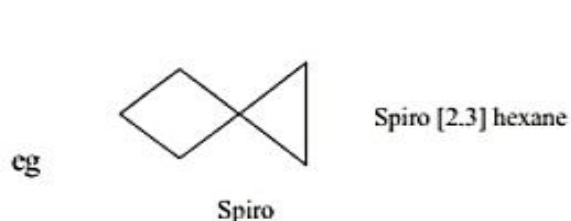


Spiro

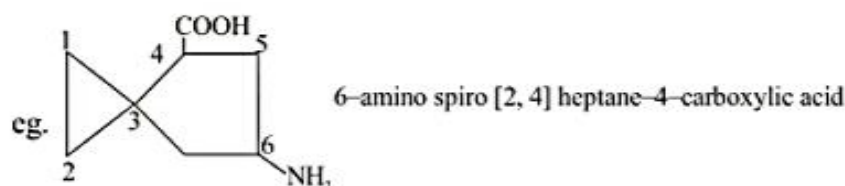
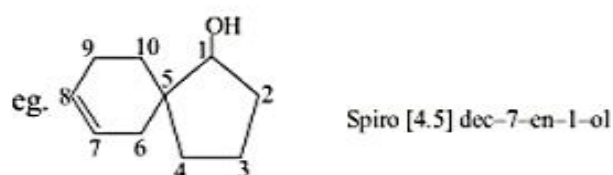




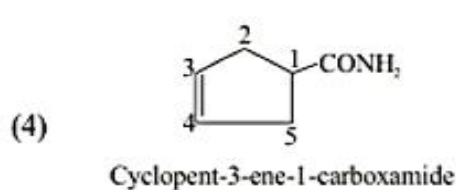
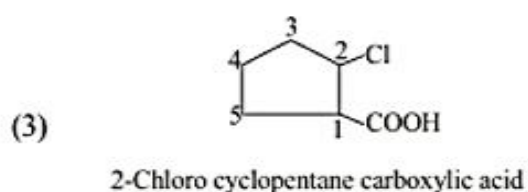
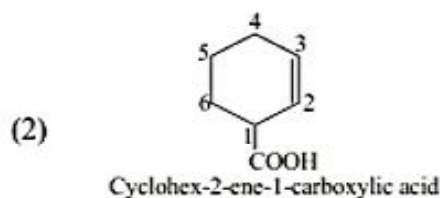
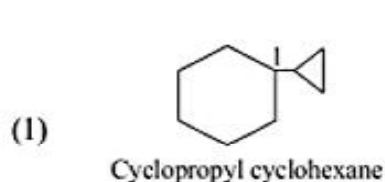
Name : Prefix + no. of carbon in bridges in increasing order + suffix  
Spiro [2. 4] heptane



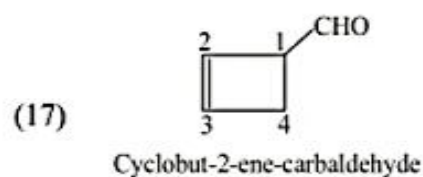
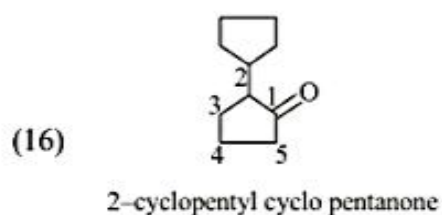
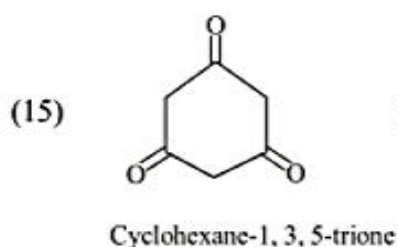
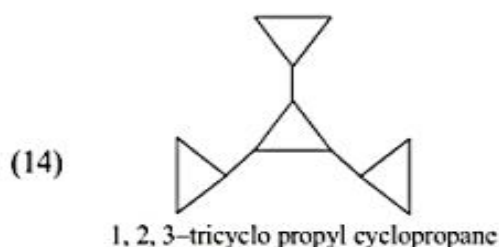
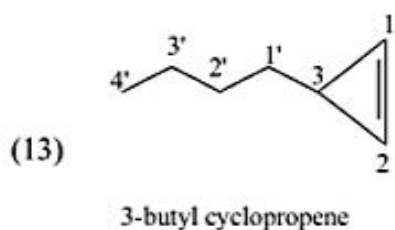
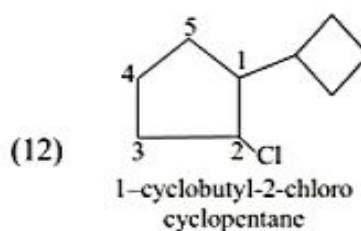
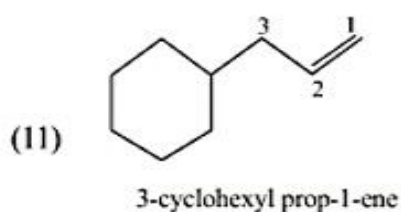
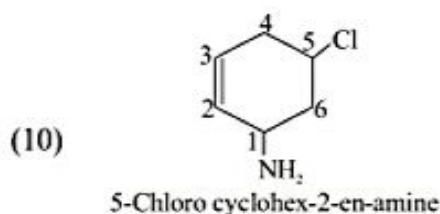
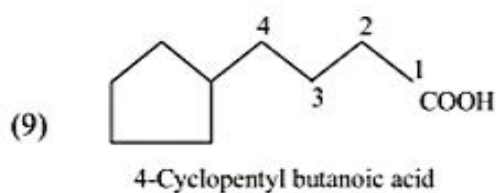
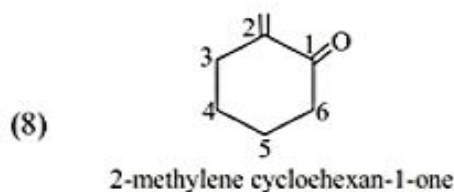
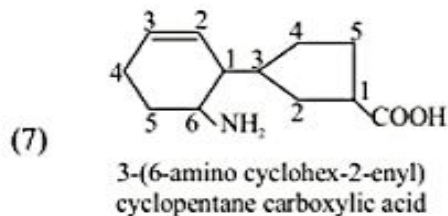
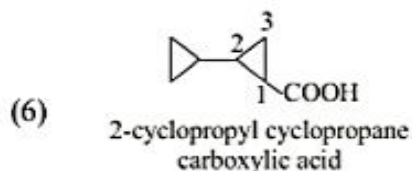
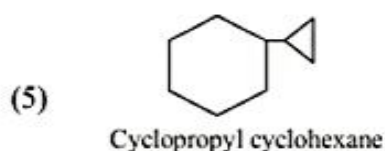
**Rule for numbering :** - In spiro compounds numbering starts from carbon of smaller ring which is next to spiro carbon proceeds towards other carbon atoms of smaller ring then towards larger ring via spiro carbon atom.



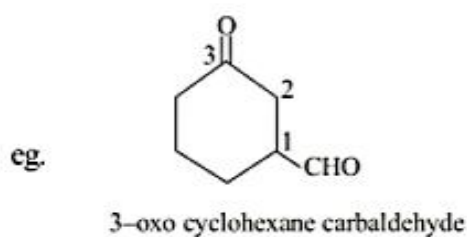
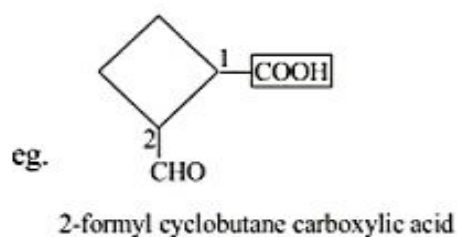
eg.





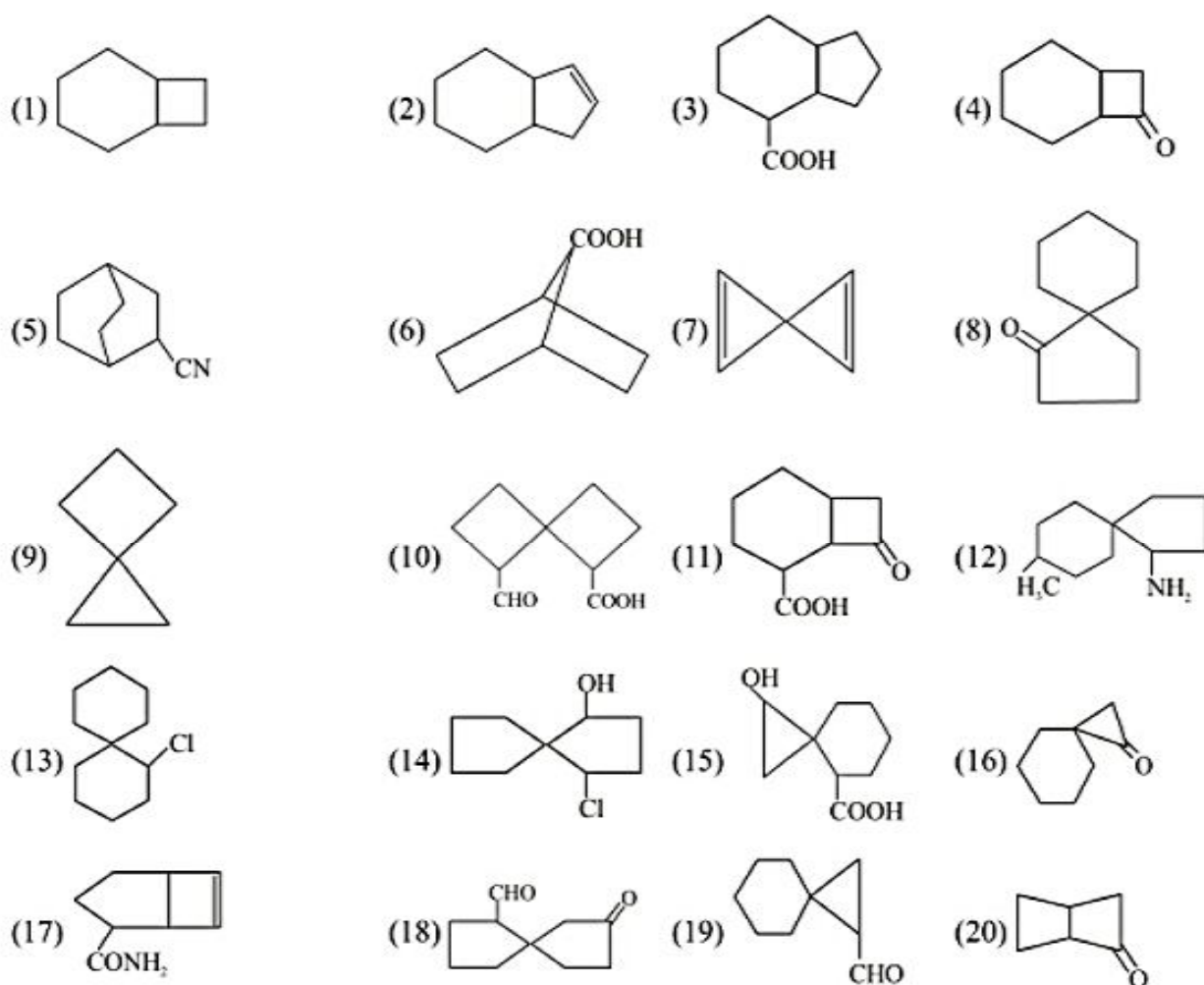


**Rule :-** If more than one functional group is present at cyclic chain, then principal function group (PFG) is selected



### PROBLEMS

Write the IUPAC Nomenclature of following compounds :



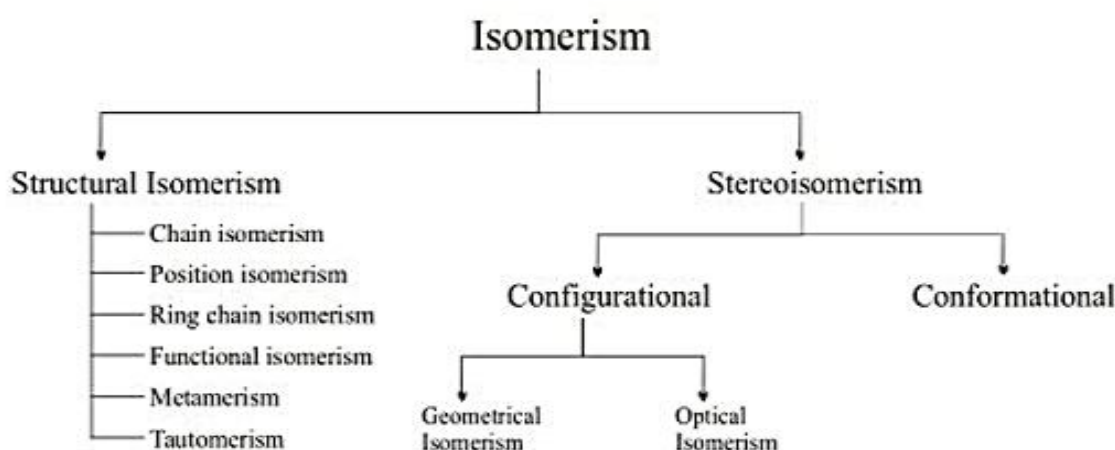
### ANSWER

- |   |   |
|---|---|
| (1) bicyclo [4.2.0] octane                          | (2) bicyclo [4.3.0] non-7-ene                       |
| (3) bicyclo [4.3.0] nonane-2-carboxylic acid        | (4) bicyclo [4.2.0] octane-7-one                    |
| (5) bicyclo [2.2.2] octane-2-carbonitrile           | (6) bicyclo [2.2.1] heptane-7-carboxylic acid       |
| (7) spiro [2.2.0] penta-1, 4-diene                  | (8) spiro [4.5] decan-1-one                         |
| (9) spiro [2.3] hexane                              | (10) 5-formyl spiro [3.3] heptane-1-carboxylic acid |
| (11) 8-oxo bicyclo [4.2.0] octane-2-carboxylic acid | (12) 8-methyl spiro [4.5] decan-1-amine             |
| (13) 1-chloro spiro [5.5] undecane                  | (14) 4-chloro spiro [4.4] nonan-1-ol                |
| (15) 1-hydroxy spiro [2.5] octane-4-carboxylic acid | (16) spiro [2.5] octan-1-one                        |
| (17) bicyclo [3.2.0] hept-6-ene-2-carboxamide       | (19) spiro [2.5] octane-1-carbaldehyde              |
| (18) 7-oxo spiro [4.4] nonane-1-carbaldehyde        |   |
| (20) bicyclo [2.2.0] hexan-2-one                    |   |

# ISOMERISM

## INTRODUCTION

- (i) The compound which have the same molecular formula but differ in physical and chemical properties are called as Isomer and the phenomenon is called Isomerism.
- (ii) The term 'isomer' was given by Berzellius.
- (iii) The isomer was derived from Greek word meaning 'equal or like part' (isos= equal; meros = parts)

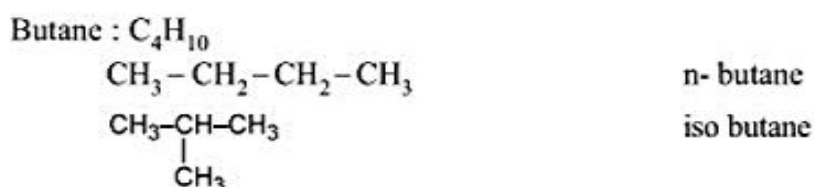


## (I) STRUCTURAL ISOMERISM / CONSTITUTIONAL ISOMERISM

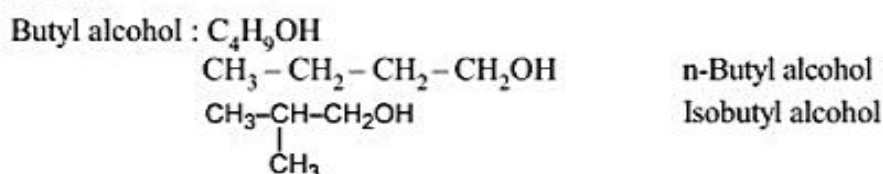
Structural isomers possess the same molecular formula but different connectivity of atoms. The term constitutional isomerism is a more modern term of structural isomerism. It is sub-classified into following types.

### (i) Chain Isomerism :

The different arrangement of carbon atoms gives rise to chain isomerism. Chain isomers possess different lengths of carbon chains (straight or branched). Such isomerism is shown by each and every family of organic compounds.



n-butane has the chain of four carbon while isobutane has three in carbon chain. Hence they are chain isomers.

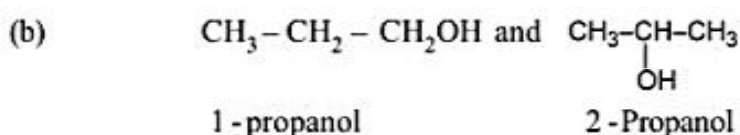
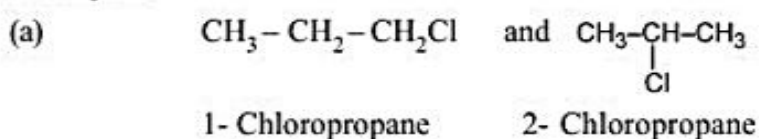


These two butyl alcohols are chain isomers.

To show position isomerism following conditions must be followed

- (i) The same molecular formula
- (ii) The same length of carbon chain
- (iii) The same functional group.

**Example :**

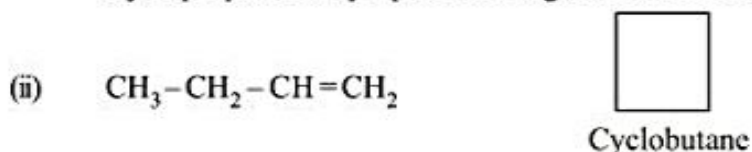


(iii) **Ring chain isomerism**

Such isomerism arises because of the difference of carbon-chain or ring.  
For example :



Cyclopropane and propene are ring chain isomers.

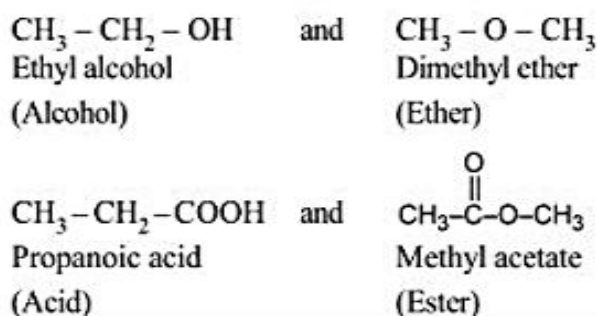


Cyclobutane is the ring-chain isomer of 1-butene.

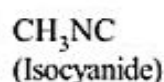
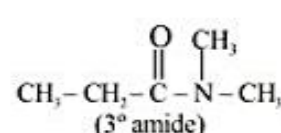
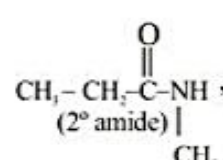
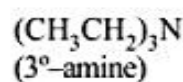
**Note: Acyclic Alkanes do not exhibit ring-chain isomerism.**

**(iv) Functional group isomerism**

Compounds with the same molecular formula but differing in the type of functional group they possess are classed as functional isomers and isomerism between them is known as functional isomerism. For example:



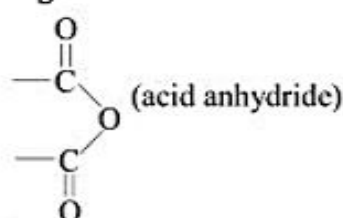
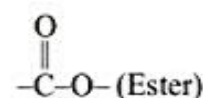
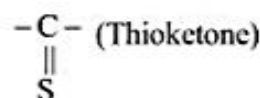
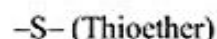
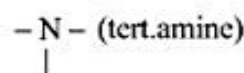
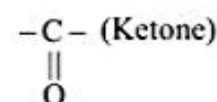
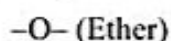




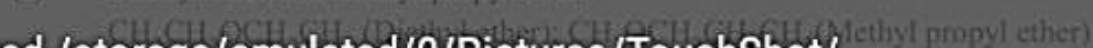
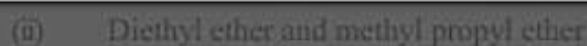
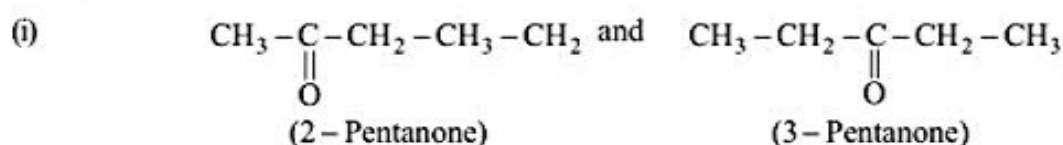
(v) **Metamers :**

This type of Isomerism arises due to unequal distribution of alkyl substituents around a polyvalent functional group.

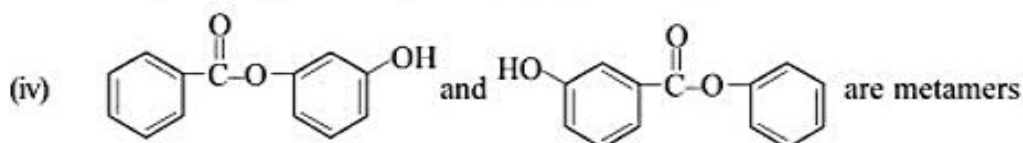
Some example of Polyvalent functional groups.



**Example :-**



- (iii) Diethyl amine and methyl propylamine  
 $\text{CH}_3\text{CH}_2 - \text{NH} - \text{CH}_2\text{CH}_3$  (Diethyl amine);  
 $\text{CH}_3\text{CH}_2\text{CH}_2 - \text{NH} - \text{CH}_3$  (Methyl propyl amine)



(vi) **Tautomerism :**

- Tautomerism is a special type of functional group isomerism which arises due to the transfer of hydrogen atom as proton from a polyvalent atom to other polyvalent atom.
- Such isomers are directly and readily inter convertible under ordinary conditions, and the isomers are called tautomers.
- Tautomers exist in dynamic equilibrium.
- The other names of tautomerism are 'desmotropism' or 'prototropy'.
- Tautomerism is thus the property shown by certain compounds exhibiting different properties, as if they possess different structures and these constitutional isomers are called tautomers.
- If the hydrogen atom oscillates between two polyvalent atoms linked together, the system is called as *Diad*.



- (vii) Hydrogen atom oscillates in between first and third atoms in a chain, the system is called as triad.



(a) **Keto - Enol Tautomerism -**

- When the tautomers exist in the two forms keto & enol then, such type of tautomerism is called keto-Enol tautomerism'.
- It was discovered by the scientist 'Knorr' in 1911 in acetoacetic ester.
- The Keto means the compound has a Keto group  $> \text{C} = \text{O}$ , and the enol form has both double bond and OH (hydroxy) group joined to the same carbon.

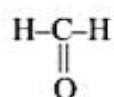


**Conditions for tautomerism**

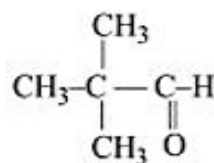
- Presence of groups like  $> \text{C} = \text{O}$ ,  $-\text{N} = \text{O}$ ,  $> \text{C} = \text{N}-$  &  $\alpha\text{-H}$  with respect to these groups.
- In order for conversion of a keto form to its enol form it must have an  $\alpha$ -hydrogen (i.e., hydrogen attached to the carbon adjacent to the carbonyl group). Thus benzaldehyde, m-chlorobenzaldehyde (in general, aromatic aldehydes) formaldehyde, trimethylacetaldehyde do not exist as their enol forms.



Benzaldehyde m-Chlorobenzaldehyde



Methanal



Trimethyl-acetaldehyde

- (iii) Keto enol tautomerism can occur both in acidic and basic medium.

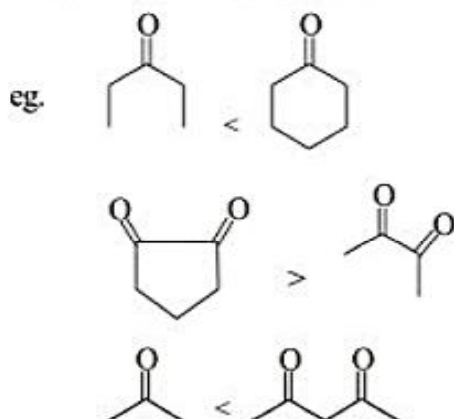
**Example of Keto enol tautomerism :-**

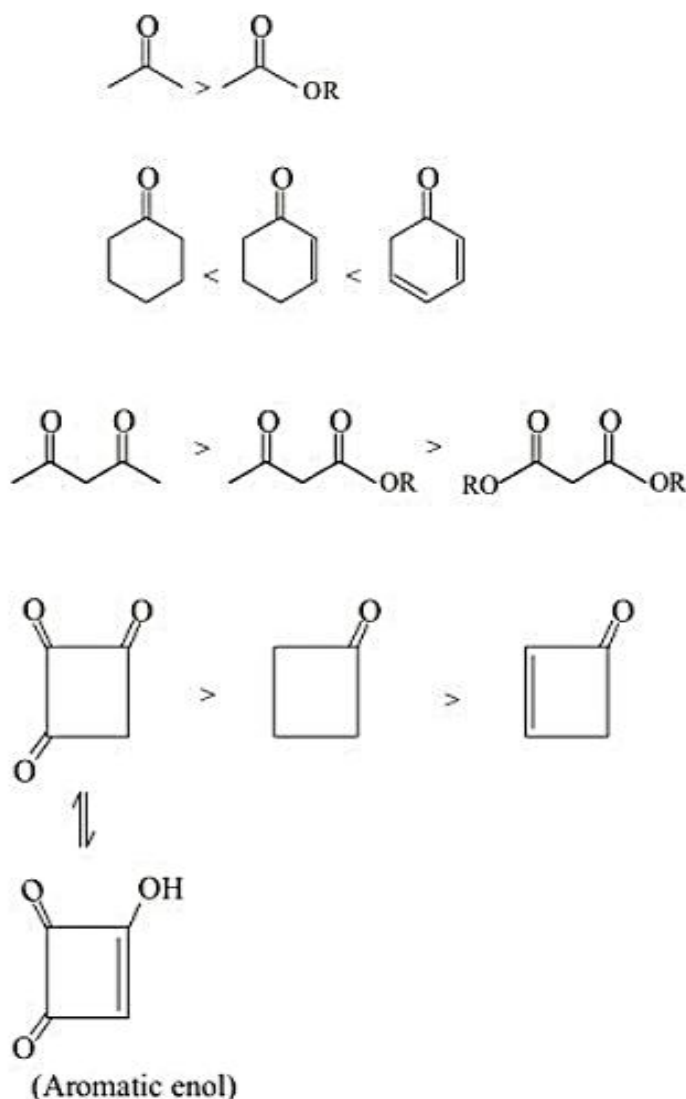


**Enol – Contents :** It is the % amount of enol in keto enol system usually keto content is generally more than Enol. contents.

Enol contents:  $\propto$  Stability of enol  
 $\propto$  aromatic in enol  
 $\propto$  conjugation in enol  
 $\propto$  Hydrogen bonding in enol  
 $\propto$  Acid strength of  $\alpha$ -H of keto form  
 $\propto$  Presence of electron withdrawing group

Normally Enol content of cyclic system is greater than corresponding a cyclic system as insertion of  $\pi$ -bond is easier in cyclic system.





### MCQ

- Q.1**  $\text{CH}_3\text{CH}_2\text{CH}_2\text{-Cl}$  and  $\text{CH}_3\text{-}\underset{\text{Cl}}{\text{CH}}\text{-CH}_3$  shows which type isomerism  
 (A) Chain isomers (B) Position isomers  
 (C) Functional isomers (D) Metamers
- Q.2**  $\text{CH}_3\text{CH}_2\text{CH}_2\text{-OH}$  and  $\text{CH}_3\text{-}\underset{\text{OH}}{\text{CH}}\text{-CH}_3$  shows which type of isomerism  
 (A) Chain isomers (B) Position isomers (C) Functional isomers (D) Metamers
- Q.3**  $\text{CH}_3\text{CH}_2\text{OH}$  and  $\text{CH}_3\text{-O-CH}_3$  express which type of isomerism  
 (A) Functional isomers (B) Chain isomers (C) Metamers (D) Position isomers



Q.4  $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_3$  and  $\text{CH}_3\text{-CH(CH}_3\text{)-CH}_3$  shows which type of isomerism



(A) Chain isomer (B) Position isomer (C) Functional isomer (D) Metamers

Q.5 Alcohol and ether express which type of Isomerism

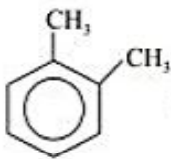
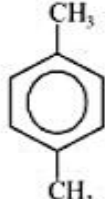
(A) Position isomers (B) Chain isomers (C) Metamers (D) Functional isomers

Q.6 How many position isomers are shown by  $\text{CH}_3\text{-CH=CH-CH}_3$

(A) 2 (B) 3 (C) 4 (D) 5

Q.7 How many position isomers are shown by  $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-NH}_2$


(A) 5 (B) 3 (C) 4 (D) 2

Q.8  and  shows which type of isomerism.


(A) Position isomers (B) Chain isomers (C) Functional isomers (D) Metamers

Q.9 How many Ring chain isomers are possible for  $\text{C}_3\text{H}_6$ .

(A) 2 (B) 3 (C) 4 (D) 5

Q.10  $\text{CH}_3\text{-CH}_2\text{-CH=CH}_2$  and  express which type isomerism.

(A) Ring chain isomers (B) Metamers (C) Position isomers (D) Chain isomers

Q.11  $\text{CH}_3\text{-CH=CH}_2$  and  express which type of isomerism

(A) Ring chain isomers (B) Chain isomer (C) Position isomers (D) Metamers

Q.12  $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$ ,  $\text{CH}_3\text{CH}_2\text{NHCH}_3$  and  $\text{CH}_3\text{-N(CH}_3\text{)-CH}_3$  express which of Isomerism



(A) Functional Isomers (B) Chain Isomers (C) Metamers (D) Position isomers

Q.13  $\text{CH}_3\text{CH}_2\text{COOH}$  and  $\text{CH}_3\text{-C(=O)-O-CH}_3$  express which of isomerism

(A) Position isomers (B) Chain Isomers (C) Metamers (D) Functional Isomers

Q.14 Alkynes and Alkadienes express which type of isomerism

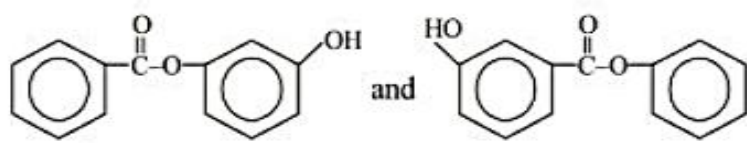
(A) Position isomers (B) Chain isomers (C) Metamers (D) Functional isomers

Q.15 The type of isomerism observed in urea and  $\text{NH}_2\text{-CH=NOH}$

(A) Chain isomers (B) Position isomers  
(C) Geometrical isomers (D) Functional isomers

- Q.16  $\text{CH}_3\text{-CH}_2\text{-O-CH}_2\text{CH}_3$  and  $\text{CH}_3\text{-O-CH}_2\text{CH}_2\text{CH}_3$  express which type of Isomerism  
 (A) Metamers (B) Functional isomers (C) Tautomerism (D) Functional isomers

- Q.17  $\text{CH}_3\text{-}\overset{\text{CH}_3}{\underset{\text{O}}{\parallel}}{\text{C}}\text{-CHCH}_3$  and  $\overset{\text{CH}_3}{\text{CH}_2}\text{-}\overset{\text{O}}{\parallel}{\text{C}}\text{-CH}_2\text{CH}_3$  express which type isomerism  
 (A) Metamers (B) Tautomers (C) Functional isomers (D) Position isomers

- Q.18  express which type of isomers  
 (A) Metamers (B) Tautomers (C) Functional Isomers (D) Chain Isomers

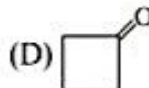
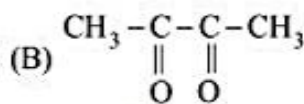
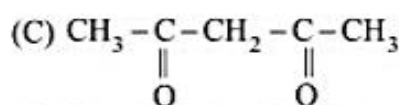
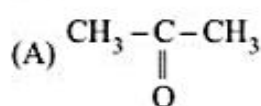
- Q.19 Diethyl amine and methyl propyl amine express which type of Isomers.  
 (A) Functional isomers (B) Position isomers (C) Metamers (D) Chain isomers

- Q.20 The molecules which exhibit metamerism are  
 (A)  $\text{C}_4\text{H}_{10}\text{O}$  (ethers) (B)  $\text{C}_4\text{H}_8$  (alkene) (C)  $\text{C}_5\text{H}_{10}\text{O}$  (ketone) (D)  $\text{C}_4\text{H}_{11}\text{N}$  (amine)

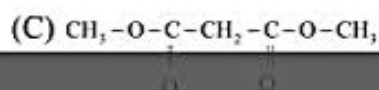
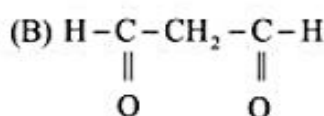
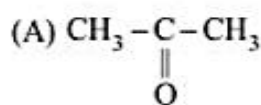
- Q.21 Which molecule does not express Tautomerism  
 (A)  $(\text{CH}_3)_3\text{CCHO}$  (B)  $\text{CH}_3\text{CHO}$  (C)  $\text{CH}_3\text{-}\overset{\text{O}}{\parallel}{\text{C}}\text{-CH}_3$  (D)  $\text{CH}_3\text{-CH}_2\text{CHO}$

- Q.22 Which form is more stable for  $\text{CH}_3\text{-}\overset{\text{O}}{\parallel}{\text{C}}\text{-CH}_3$   
 (A) enol-form (B) keto form  
 (C) both form are equally stable (D) keto and enol form does not exist

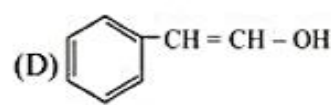
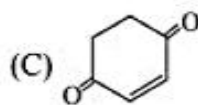
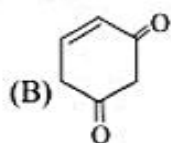
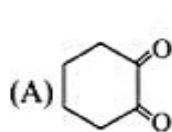
- Q.23 Which molecule has higher enol content



- Q.24 Which molecule has higher keto-contents



Q.25 Which of the following compounds can exhibit tautomerism



Q.26 The number of structural isomer shown by  $C_6H_{14}$

(A) 6

(B) 5

(C) 6

(D) 8

Q.27 How many chain isomers are shown by  $C_4H_{10}$

(A) 3

(B) 2

(C) 4

(D) 5

Q.28 How many chain isomers are shown by  $C_4H_9OH$

(A) 2

(B) 3

(C) 4

(D) 5

Q.29 Number of structural of isomers shown by  $C_6H_{14}$  :

(A) 4

(B) 5

(C) 8

(D) 6

### ANSWERS

Q.1	B	Q.2	B	Q.3	A	Q.4	A	Q.5	D	Q.6	A
Q.7	D	Q.8	A	Q.9	A	Q.10	A	Q.11	A	Q.12	A
Q.13	D	Q.14	D	Q.15	D	Q.16	A	Q.17	A	Q.18	A
Q.19	C	Q.20	A, C, D	Q.21	A	Q.22	B	Q.23	C	Q.24	B
Q.25	A, B, C, D	Q.26	B	Q.27	B	Q.28	A	Q.29	B		

## (II) STEREOISOMERISM / SPACE ISOMERISM

Compounds having same molecular formula, same connectivity and structural formula but differ due to spatial arrangement of group or atom are said to be stereo isomers and phenomenon is termed as stereoisomerism.

It is divided into two parts : (1) Configuration isomerism (2) Conformational isomerism

1. **Configuration isomerism** : Stereoisomers which are not interconvertible at room temperature are known as configurational isomers

Configurational isomerism is further divided into two parts

(A) Geometrical isomerism

(B) Optical isomerism

### GEOMETRICAL ISOMERISM

It is type of configurational isomerism which arises due to restricted rotation of atoms or groups around a double bonded system or cyclic system.

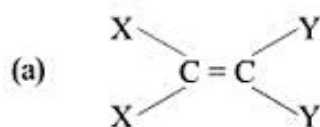
#### Conditions

(i) Restricted rotation

(ii) Different functional groups or atoms which is showing geometrical isomerism.

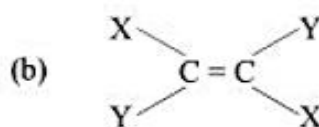


For example:



Not showing G.I.

(Because same group X and Y present on each carbon)

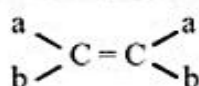


Showing G.I.

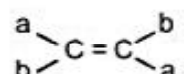
Geometrical isomers are named as

(a) cis- trans isomers (b) E and Z isomers (c) Syn-anti isomers

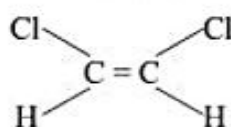
- (a) *Cis- trans isomers.* When like atoms or groups attached at the same side of double bonded C-atom-called as cis. isomers. When like atoms or groups are on the opposite sides of doubly bonded carbon, are called. trans isomers.



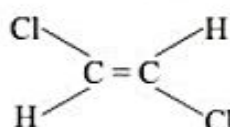
cis isomers



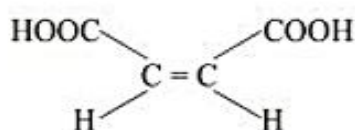
trans isomers



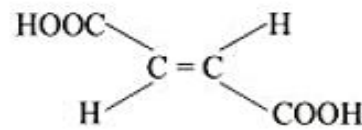
cis isomer



trans isomer



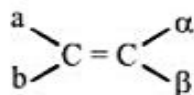
Maleic acid  
(cis isomer)



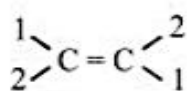
Fumaric acid  
(trans isomer)

- (b) E and Z isomers,

- (i) The above system is used for derivatives of alkenes in which all the four substituents should be different



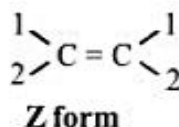
- (ii) Following a set of rules (Cahn - Ingold-Prelog rules) the substituents on a double bond are assigned priorities.
- (iii) The double bond is assigned the configuration E (From entgegen, the german word for opposite) if the two groups of higher priority are on the opposite sides of the double bond.



E form

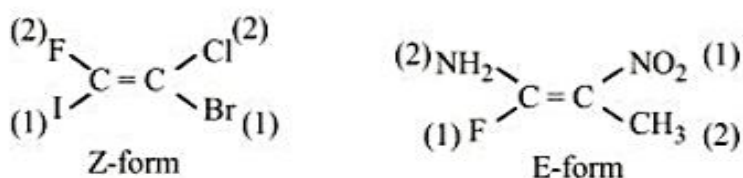
- (iv) On the other hand, the double bond is assigned the configuration Z (From zusammen, the German word for together) if the two groups of higher priority are on the same side of the double bond.



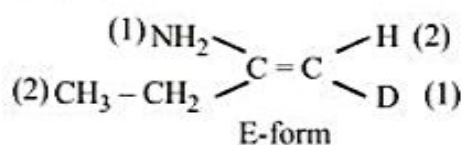


**Priority rule : cahn, ingold & prelog** proposed a sequence rule.

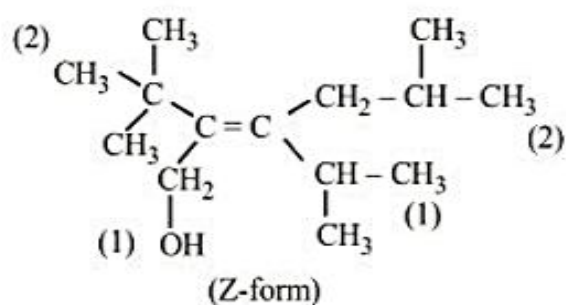
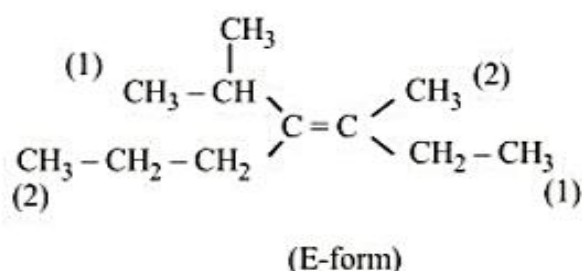
**Rule-1** When atom or group of atom which are directly attach to the stereogenic centre have higher atomic number will have higher priority. Example



**Rule-2** When the atomic number will be same, priority assigned on basis of atomic weight.



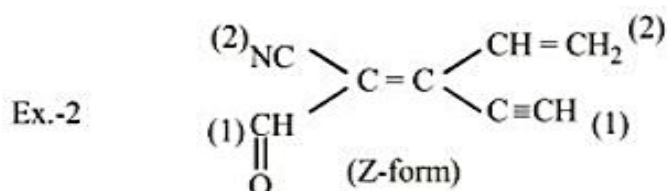
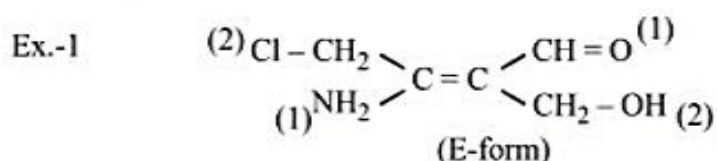
**Rule-3** When both atomic number and atomic weight are same then priority will be decided by the next joining atom.



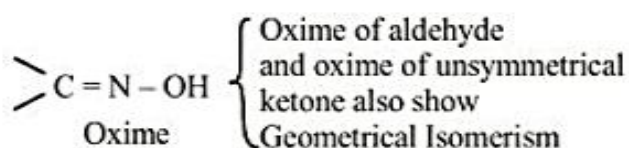
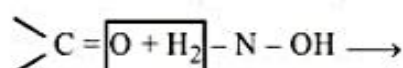
**Rule-4** If multiple bonded group attach to the double bonded carbon, then they are considered in following manner.



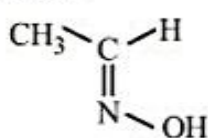
For example :



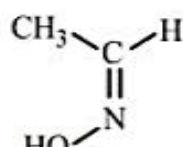
- (c) **Syn-anti isomers** This type of isomerism exhibit by oximes and Azo compound. Oximes are the compounds formed by the reactions of aldehydes or ketones with hydroxyl amine. The products obtained have all the necessary conditions for Geometrical isomerism. i.e. restricted rotation they can be represented by the general formula



Aldoximes

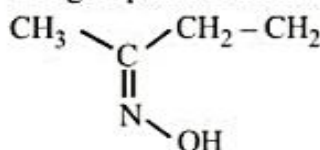


Syn form

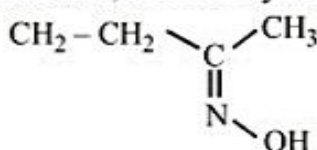


Anti form

When -OH group and H atom is same side, then it is syn form otherwise anti form



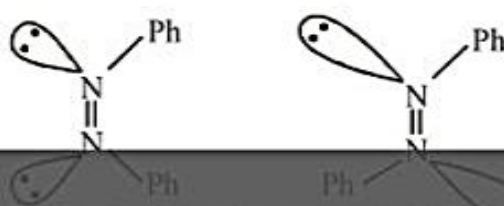
Syn form



Anti form

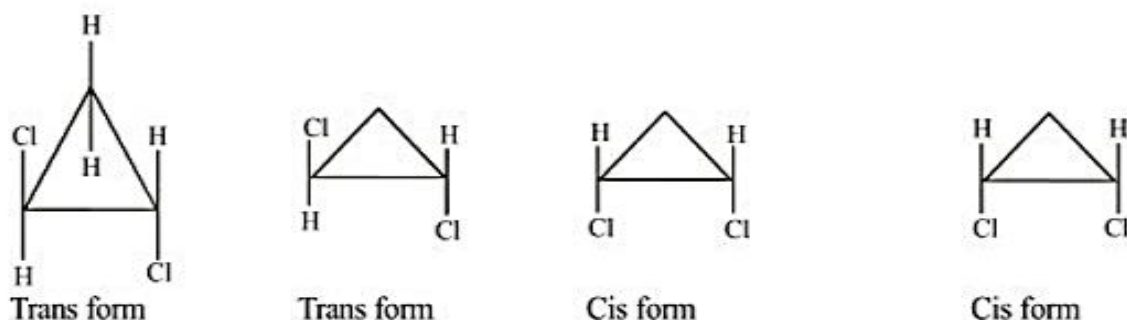
In unsymmetrical Ketoxime, if -OH and the alphabetically alkyl present on the same side of double bond, then it is called as syn form and other isomer is anti form

**Geometrical Isomerism in Azo compound :**



### Geometrical Isomerism in cyclo alkane :

In cyclic compound the rotation about C – C single bond is not free because of the rigidity caused by the presence of other carbon of the ring which keep them tightly held, thus a disubstituted cyclic compound (having the two substitution at the separate carbon) will also show Geometrical Isomerism. The substituents on the same side are cis-isomers while the substituents on opposite sides represent trans-isomers.



### No. of geometrical isomers in polyenes :

**Case-1** In case of unsymmetric alkene. If  $R_1 \neq R_2$  ( $R_1 - CH = CH - CH = CH - R_2$ )

$$\text{no. of G.I.} = 2^n$$

$n \rightarrow$  number of double bond showing geometrical isomerism

Ex.-  $CH_3 - CH = CH - CH = CH - CH_2 - CH_3$

$$N = 2^n = 2^2 = 4.$$

**Case-2** In case of symmetric alkene. If  $R_1 = R_2$  ( $R_1 - CH = CH - CH = CH - R_2$ )

$$\text{no. of G.I.} = 2^{n-1} + 2^{p-1}$$

if  $n$  is even no. then,  $P = \frac{n}{2}$

if  $n$  is odd no. then,  $P = \frac{n+1}{2}$

Ex.-  $CH_3 - CH = CH - CH = CH - CH = CH - CH_3$

$$\text{here } \begin{cases} n = 3 \\ P = \frac{3+1}{2} \end{cases}$$

$$N = 2^2 + 2^1 = 6$$

### MCQ

**Q.1** Which of the following compounds exhibits geometrical isomers -

- (A)  $C_2H_5Br$                       (B)  $(CH_2)(COOH)_2$     (C)  $CH_3CHO$                       (D)  $(CH_2)_2(COOH)_2$

**Q.2** The number of geometrical isomers of

$CH_3CH = CH - CH = CH - CH = CHCl$  is -

- (A) 2                      (B) 4                      (C) 6                      (D) 8



- Q.3 Maleic and fumaric acids are:  
 (A) Geometrical isomer (B) Tautomers (C) Optical isomers (D) Metamers
- Q.4 Which of the following can exhibit cis-trans isomerism –  
 (A)  $\text{HC} = \text{CH}$  (B)  $\text{ClCH} = \text{CHCl}$  (C)  $\text{CH}_3\text{CHClCOOH}$  (D)  $\text{ClCH}_2 - \text{CH}_2\text{Cl}$
- Q.5 Geometrical isomerism is possible in case of:  
 (A) Pent-2-ene (B) Butane (C) 2-Butene (D) Ethene
- Q.6 Give the E-Z designation of the following compound -
- 
- (A) E (B) Z (C) E-Z (D) E-E
- Q.7 Which of the following compounds will exhibit trans (geometrical) isomerism?  
 (A) 2-butene (B) 2-butyne (C) 2-butanol (D) butanal

### ANSWERS

Q.1	B	Q.2	D	Q.3	A	Q.4	B	Q.5	A, C	Q.6	A
Q.7	A										

## OPTICAL ISOMERISM

Configurational isomers which differ in their optical activity.

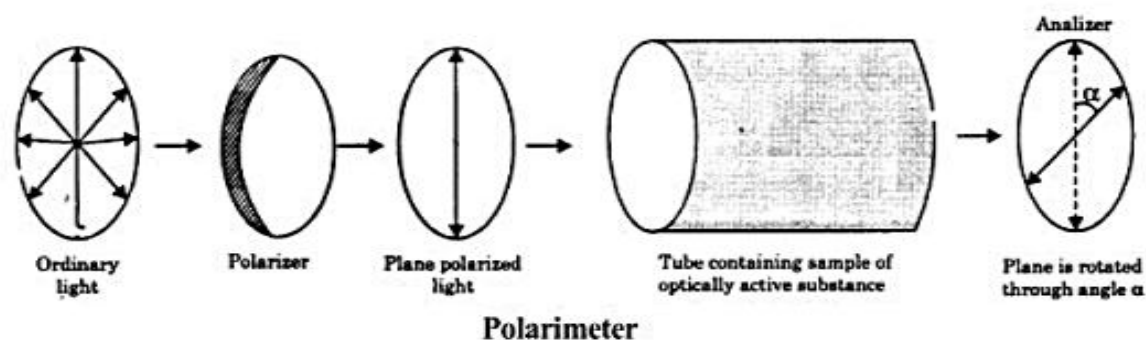
**Optical Activity :** The ability of optically active substances to cause rotation in the plane of oscillations of polarized light is called optical activity. The substances which do not have any interaction with plane polarized light are called optically inactive substances.

Following experiment was conducted to determine the optical activity of a substance

- Under ordinary conditions, the light waves oscillate in infinite number of planes passing through the line of propagation at right angle.
- Plane polarized light is a light whose vibrations take place in only one of these possible planes.
- Ordinary light can be turned into plane polarized light by passing it through Nicol prism (made up of calcite, a special crystalline form of  $\text{CaCO}_3$ )
- When plane polarize light is passed through the liquid or dissolved state of such substances.
- The plane of oscillation gets rotated through some angle towards left or right of the original plane of oscillations. The substances which rotate the plane of polarized light are called optically active substances.
- The substances which rotate the plane of polarized light in the clockwise direction, i.e., towards right are called dextrorotatory substances (Latin : dextro means right). This is indicated by putting a better d or (+) sign before the name of the substances.
- The substances which rotate the plane of polarized light in the anticlockwise direction, i.e., towards left are called leavorotatory substances (Latin : laevus means left). This is indicated by putting letter 'l' or (-) sign before the name of the substance.

(h) The angle through which the plane of polarized light is rotated is represented by  $\alpha$  and is called observed angle of rotation.





(i) The amount of rotation caused by an optical active compound depends on various factors-

- (a) Wavelength of light beam
- (b) Temperature
- (c) Density or concentration
- (d) Length of the solution through which light beam has been passed.

**Specific Rotation :** The specific rotation of optically active compound can be defined as the amount of optical rotation observed when plane polarised light is passed through a solution of 1 gm per ml concentration solution in a 1 dm long tube.

$$\text{Specific rotation} = [\alpha]_D^t = \frac{\alpha}{l \times C}$$

#### Cause of optical activity:-

- (a) In order to exhibit optical activity, an object or molecule must be chiral.
- (b) Any molecule or object is said to be chiral if does not have any element of symmetry i.e. a plane of symmetry or a centre of symmetry.

**Plane of symmetry:-** A 'Plane' of symmetry' is a plane which divides an object in such a way that the part of it on one side of the plane is the mirror image of that on the other side for eg. a ball is symmetrical while a hand is asymmetric



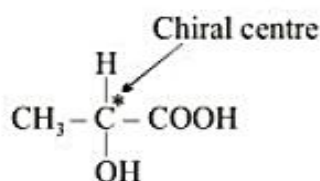
A chiral molecule or object is non-super imposable on its mirror images.

- (c) Hence, chiral objects or molecules are also called dissymmetric objects or molecules the word chiral in fact is derived from the Greek word cheir, meaning hand.

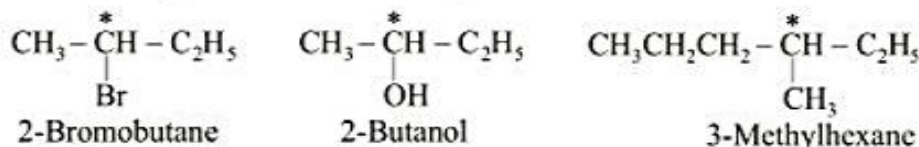
#### Chiral centre:-

(i) A carbon atom bonded to four different atoms / groups in the molecule is called Chiral centre.

(ii) The chiral centre in the molecule is represented by asterisk (\*). For example, the second carbon in lactic acid is chiral centre because it is bonded to four different groups (– H, – CH<sub>3</sub>, – OH and – COOH).

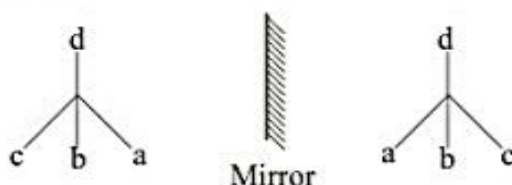


(iii) Some more examples of molecules having one chiral centre are



- (d) Compounds which are mirror images of each other and are not superimposable are termed *enantiomers* and the phenomenon is described as *enantiomerism*.

**Enantiomers :** Enantiomers are molecules which are mirror images of each other i.e. they should be non-superimposable.



#### Characteristics of Enantiomers :

Some of the important characteristics of enantiomers are as given below :

- (i) Enantiomers have identical physical properties such as melting point, boiling point, density, refractive index etc.
- (ii) Enantiomers are optically active substances. They rotate the plane of polarized light in opposite directions but to the equal extent.
- (iii) Enantiomers have identical chemical properties. This means that they form same products as a result of chemical combination. However, their reactivity, i.e., rates of reaction with other optically active substances are different.
- (iv) Enantiomers have different biological properties. For example (+) -sugar plays significant role in animal metabolism. On the other (–) -sugar does not play any role in metabolism.

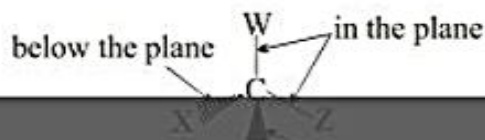
#### Representation of Enantiomers :

(a) Wedge and dash formulae

(b) Fischer Projection Formulae

##### (a) Wedge and dash formulae :

- (i) In this method, the four groups bonded to the chiral centre are represented by different means.
- (ii) A normal line represents the bond lying in the plane of paper.
- (iii) A broken line represents the bond going behind the plane of the paper and a solid wedge represents the bond projected out towards the viewer.



**(b) Fischer Projection Formulae**

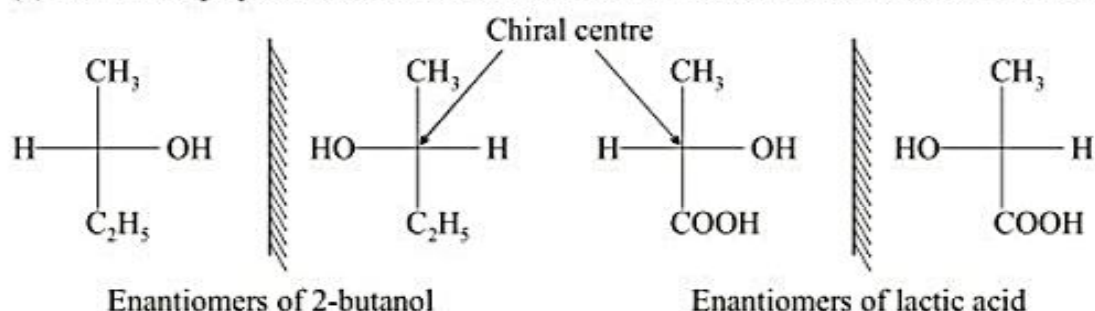
(i) Emily Fischer devised a most simple and convenient method to represent the three dimensional arrangement of groups bonded to chiral centre.

(ii) He used the point of intersection of two perpendicular lines to represent the chiral centre.

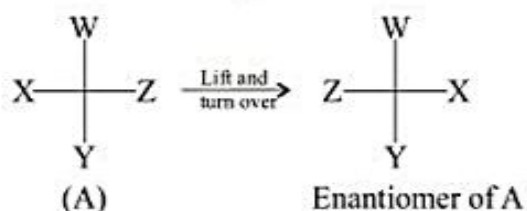
(iii) Horizontal lines represent the bonds projected out of the plane of the paper towards viewer.

(iv) Vertical lines on the other hand, represented the bonds projected back from the plane of the paper away from the viewer.

(v) The Fischer projection formulae of enantiomers of 2-butanol and lactic acid are as under

**Important Points About Fischer Projection Formula :**

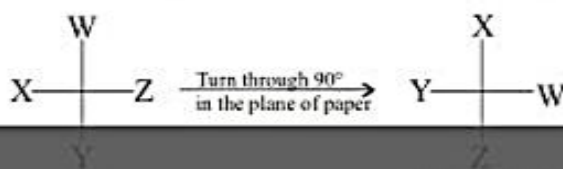
- (1) Fischer projection of a stereoisomer must not be lifted from the plane of the paper and turned over. Such an operation would result into an arrangement which is enantiomer of the original stereoisomer.



- (2) Fischer's projection can be rotated in the plane of the paper about the chiral centre through  $180^\circ$  or its whole number multiple. Such an operation produces the same arrangement



- (3) Fischer projection should not be turned in the plane of the paper through angle of  $90^\circ$  about the chiral centre. Such an operation also produces enantiomer of the original compound.



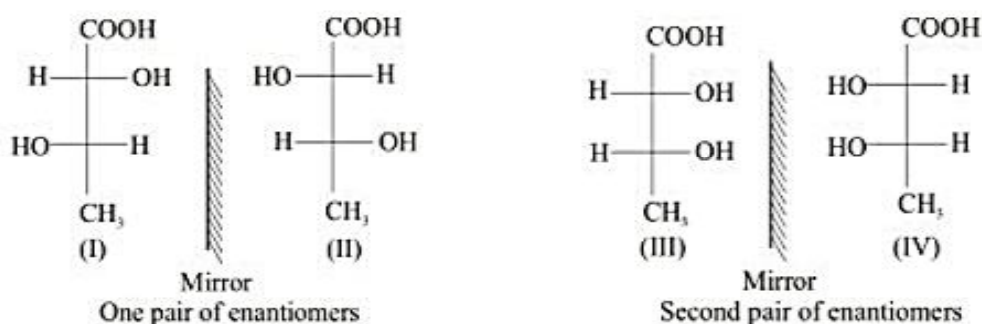


- (4) Keeping one group as steady, the other groups in the Fischer projection can be rotated clockwise or anticlockwise simultaneously. Such operation would give same arrangement as the original.



### Diastereomers :

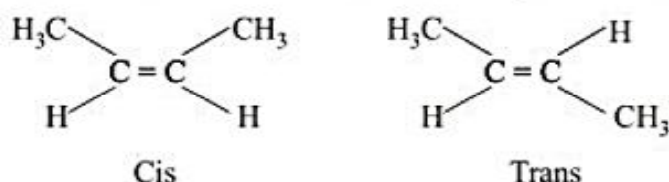
The stereoisomers which are non-superimposable and do not bear mirror image relationship are called diastereomers. For Example, a compound having two asymmetric carbon atoms can have four stereoisomers as shown below in the case of tartaric acid :



(I) is mirror image of (II); similarly (III) and (IV) are mirror images of each other. Thus, the four isomers are two pairs of enantiomers. Now compare (I) with (III); they are neither superimposable nor they are mirror images. They are called *diastereomers*. (I) and (IV) are also diastereomers, as are (II) and (III) and (II) and (IV).

### Characteristics of Diastereomers are :

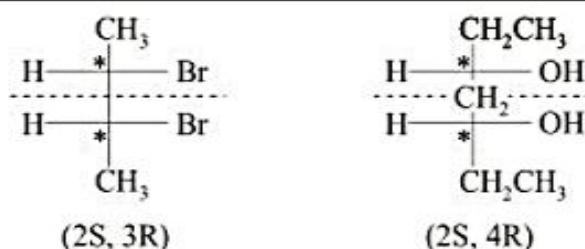
- They show similar but not identical chemical properties. The rates of reactions are different.
- They have different physical properties, such as melting points, boiling points, densities, solubilities, refractive indices, etc.
- They can be easily separated through fractional crystallization, fractional distillation, chromatography, etc.
- Diastereomers are also encountered in the case of geometrical isomers :



### MESO COMPOUND

- (a) The compounds containing two or more chiral centres but possessing achiral molecular structure because of having plane of symmetry, are called meso compounds.



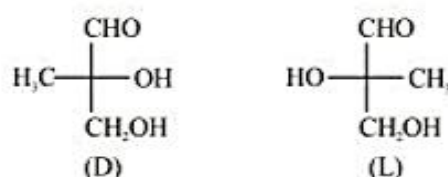


Meso Compound  
Plane of symmetry is represented by dotted line

- (b) Meso compounds do not rotate the plane of polarized light in any direction, i.e., they are **optically inactive**.
- (c) This is because of achiral nature of their molecules. Because of the present of plane of symmetry the optical rotation caused by half of the molecule is compensated by the rotation caused by the other half.
- (d) This cancellation of rotation within the molecule is referred to as **internal compensation**.
- (e) In short, the meso compounds are optically inactive due to internal compensation.

## CONFIGURATION

- (i) Three dimensional arrangement of groups about the chiral centre is called configuration
- (ii) There are two methods for assigning configuration to a molecule :
  - (a) Relative method
  - (b) Absolute method.
- (1) **Relative method of configuration (D, L System) :**
  - (a) It uses D-Glyceraldehyde and L-Glyceraldehyde as the basis for the configuration determination.
  - (b) The stereochemical descriptor D refers to the arrangement in which –OH group attached to the chiral centre is on the right side of Fischer projection, whereas descriptor L refers to arrangement in which –OH group is on the left side of the Fischer projection of glyceraldehyde.



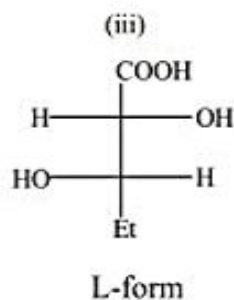
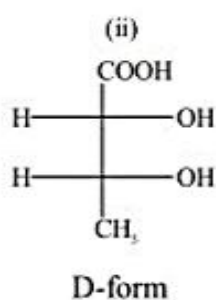
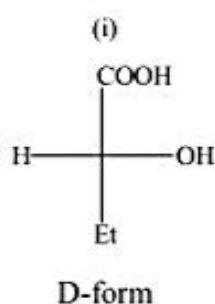
- (d) This method was found suitable for the study of optically active sugars as the sugars are defined as *poly hydroxy aldehydes and ketones*.
- (e) Glyceraldehyde also contains hydroxy and aldehyde groups but this method cannot be used for those molecules which do not possess hydroxy aldehyde groups like CFCl BrI.
- (f) If two or more than two –OH groups are present then D, L configuration is decided on basis of –OH group of lowest chiral in the Fischer projection following Fischer projection

### Golden Rule

usually, the Fischer projection is drawn, so that the longest carbon chain in the molecule is vertical with the highly oxidised function at the top.

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Examples:



### R-S system (Absolute configuration)

R → Rectus (Right)

S → Sinister (Left)

R-S nomenclature is assigned as follow :

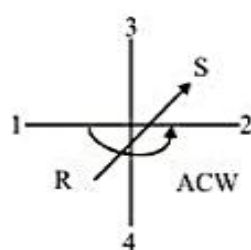
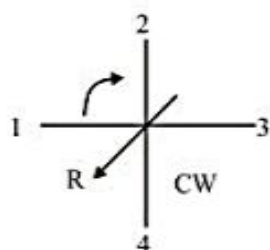
**Step-I :-** By the set of sequence rule, we give the priority order of atom or group connected through the chiral carbon.

**Step-II :-** If atom/group of minimum priority present on the vertical line, then

Movement of eyes in clockwise direction = R

Movement of eyes in anticlockwise = S

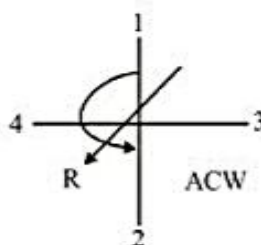
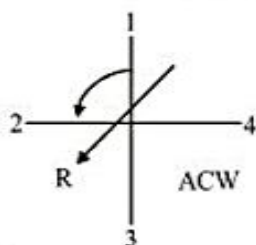
Movement of eyes taken from 1 → 2 → 3 through Low molecular weight group (if needed)



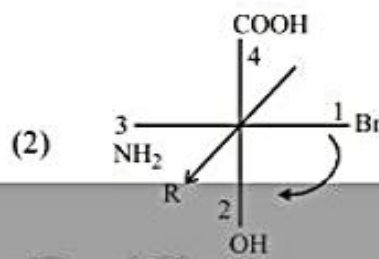
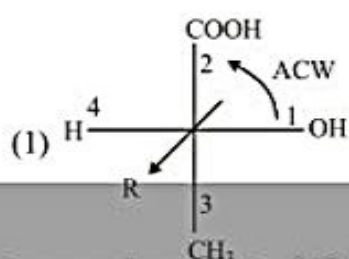
**Step III :-** If minimum priority group present on the horizontal line, then

clockwise rotation ⇒ S

anticlockwise rotation ⇒ R



Example:-



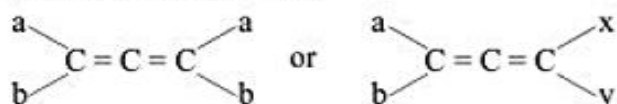
### Optical Isomerism in compound containing no chiral carbon atom

Various types of compounds belonging to this group are allenes, alkylidene cycloalkanes, spiro compounds (spiranes) and properly substituted biphenyls.

- (i) **Allenes** These are the organic compounds of the following general formula.

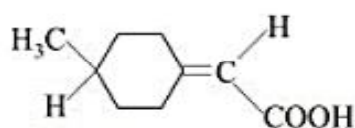


Allenes containing even number of double bonds exhibit optical isomerism provided the two groups attached to each terminal carbon atom are

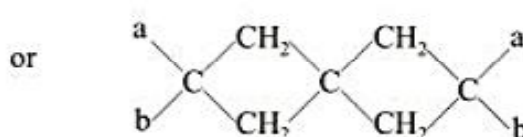


- (ii) **Alkylidene, cycloalkanes and spiro compounds :**

When one or both of the double bonds in allenes are replaced by one and two rings, the resulting systems are respectively known as alkylidene cycloalkanes and spiranes.

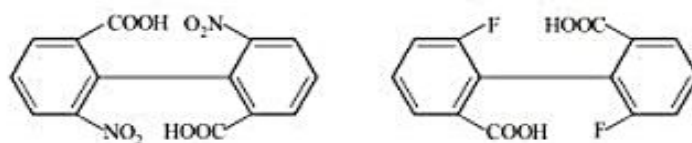


1-Methyl cyclo hexylidene-4-acetic acid  
(Alkylidene cycloalkane)



Spiranes

- (iii) **Biphenyls :** Suitably substituted diphenyl compounds are also devoid of individual chiral carbon atom, but the molecules are chiral due to restricted rotation around the single bond between the two benzene nuclei and hence they must exist in two non-superimposable mirror images of each other.



#### Number of optical isomers :

**Case - 1** When the molecule is unsymmetrical. (It cannot be divided into two halves)

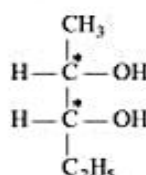
Number of *d* and *l* isomers =  $2^n$

Number of meso form = 0

Total number of optical isomers =  $2^n$

Where *n* is the number of chiral carbon atoms.

**For eg.** 2, 3 - Pentane diol



*d* and *l* isomers =  $2^2 = 4$

**Case - 2** When the molecule is unsymmetrical, number of chiral carbon = even number

Number of *d* and *l* forms =  $2^{(n-1)}$

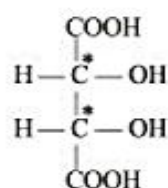
Number of meso form =  $2^{(n/2-1)}$

Total number = addition of the above

$$= 2^{n-1} + 2^{\frac{n}{2}-1}$$



For eg.: Tartaric acid



Number of d and l forms =  $2^{(n/2 - 1)} = 2$

Number of meso form =  $2^{(2/2 - 1)} = 2^0 = 1$

Total optical isomers = 3

- Case- 3.** When the molecule is symmetrical,  
 number of d and l form =  $2^{(n - 1)} - 2^{(n/2 - 1/2)}$   
 Number of meso form =  $2^{(n/2 - 1/2)}$   
 Total number of isomers =  $2^{n-1}$

## RACEMIC MIXTURE

- An equimolecular mixture of a pair of enantiomers is called racemic mixture or racemic modification.
- A racemic mixture is optically inactive. This is because of the fact that in equimolecular mixture of enantiomeric pairs, the rotation caused by the molecules of one enantiomer is cancelled by the rotation caused by the molecules of other enantiomer.
- This type of compensation of optical rotation in a racemic mixture is referred to as **external compensation**. Thus, racemic mixture becomes optically inactive because of external compensation.
- Representation of Racemic mixture : The racemic mixture of a particular sample is indicated by using the prefix (d, l) or ( $\pm$ ). For example, racemic mixture of lactic acid is represented as ( $\pm$ ) lactic acid.

## RACEMIZATION

It is a process of conversion of an optically active compound into the racemic modification. Both (+) and (–) forms of the compound are capable of racemizations under the influence of heat, light or chemical reagents.

## RESOLUTION

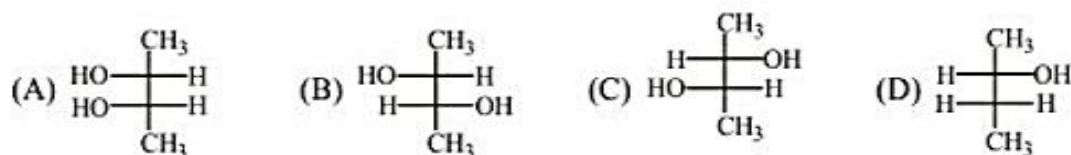
The process of separation of constituent enantiomeric forms from the racemic mixture is known as resolution.

- Chemical method :** This is probably the best method of resolution. The racemic mixture is to combine with another optically active compound and the resulting products (salt - formation) differ in properties, particularly in solubility in various solvents. By fractional crystallization from a suitable solvent, they can be separated.
- Mechanical method :** If the d and l-forms of a substance exist in well defined crystalline forms, the separation can be done by hand picking with the help of magnifying lens and a pair of tweezers.
- Biochemical method :** In this method, the resolution is done by use of micro-organisms, when certain bacteria or moulds are added to a solution of a racemic mixture, they decompose one of the optically active forms more rapidly than the other.

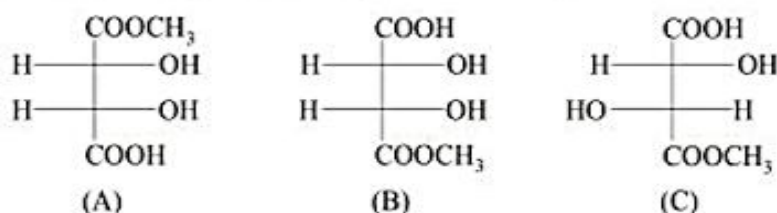


## MCQ

Q.1 A Fischer projection of (2R, 3S)-2,3-butanediol is :-



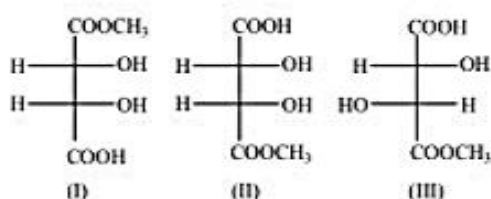
Q.2 The correct statement about the compound A, B and C.



(A) 'A' and 'B' are identical  
(C) 'A' and 'C' are enantiomers

(B) 'A' and 'B' are diastereomers  
(D) 'A' and 'B' are enantiomers

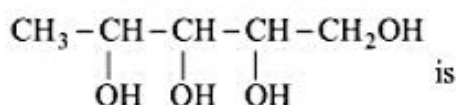
Q.3 The correct statement about the compounds I, II and III



(A) I and II are identical  
(C) I and III are enantiomers

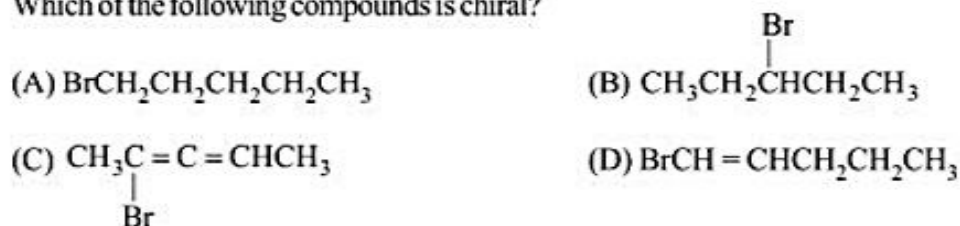
(B) I and II are diastereomers  
(D) I and II are enantiomers

Q.4 The number of optically active isomer possible for



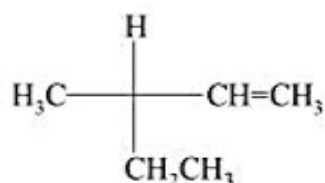
(A) 2 (B) 4 (C) 6 (D) 8 (E) 10

Q.5 Which of the following compounds is chiral?



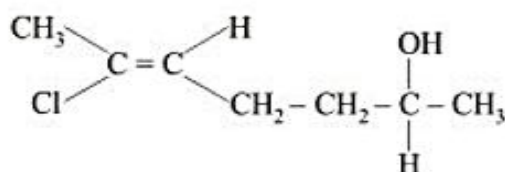
(E) None of these

Q.6 The following hydrocarbon can exhibit.



- (A) Geometrical isomerism (B) Optical isomerism  
(C) Both geometrical and optical isomerism (D) Tautomerism

Q.8 The compound whose stereochemical formula is written below exhibits x geometrical isomers and y optical isomers.



The values of x and y are

- (A) 4 and 4 (B) 2 and 2 (C) 2 and 4 (D) 4 and 2

### ANSWERS

Q.1	A	Q.2	B	Q.3	A	Q.4	D	Q.5	E	Q.6	B
Q.7	B	Q.8	B								

## 2. CONFORMATIONAL STEREOISOMERISMS

Different non-identical arrangement of atoms or group in a molecule that result by the rotation about a single bond and that can easily be reconverted at room temperature are known as conformational stereo isomers of conformers.

### Conformation isomerism :

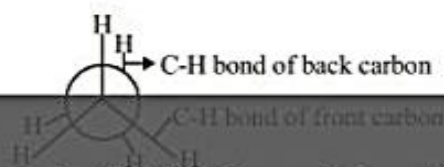
The different arrangement of atoms in space that result from the free rotation of group about C–C bond axis are called conformers, and this phenomenon is called conformation isomerism. The basic structure of the molecule various bond length and bond angle remain the same. There are infinite no. of conformers of any molecule two out of them are defined as staggered and eclipsed.

### Condition of conformation :

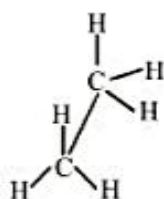
There should be three  $\sigma$ -bond present in a molecule.

### Projection of Tetrahedral Carbon Atom :

**Newman projection :** In this method the molecule is observed along the central carbon-carbon bond. a circle is drawn and centre of the circle represents the front carbon. the bonds of the front carbon are drawn from the centre of the circle while the bonds at the back carbon are drawn from the periphery.

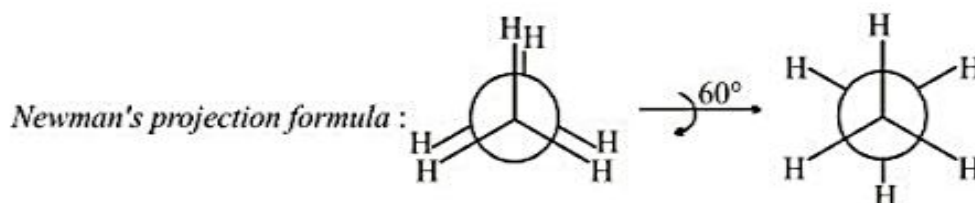
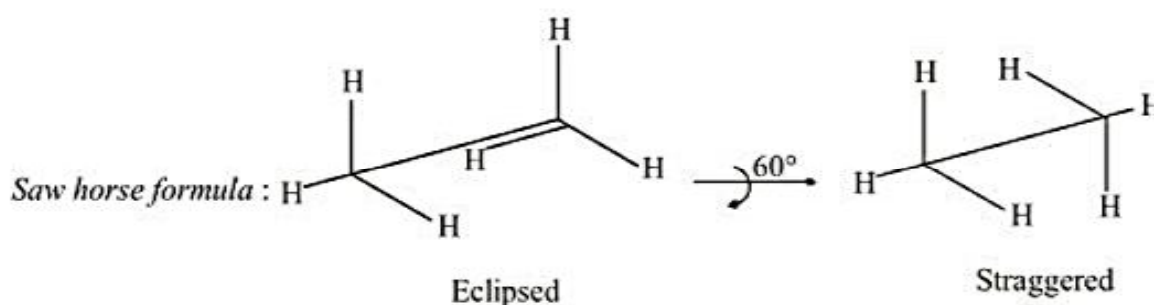


**Saw horse projection :** In this method, central carbon-carbon bond of the molecule is represented by a straight line written in bond of the molecule is represented by a straight line written in slightly tilted manner and the molecule is observed from the right side.



**Dihedral angle :-** Angle between valencies of two adjacent atoms

**Conformation in ethane ( $\text{CH}_3\text{-CH}_3$ )**

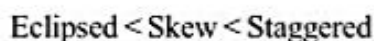


**Eclipsed form :** When H-atoms of one carbon are directly behind the other is called eclipsed form.

**Staggered form :** The hydrogen of two atoms are maximum distance with respect to one another.

**Skew form :** The different forms which exist between  $0^\circ$  to  $60^\circ$ .

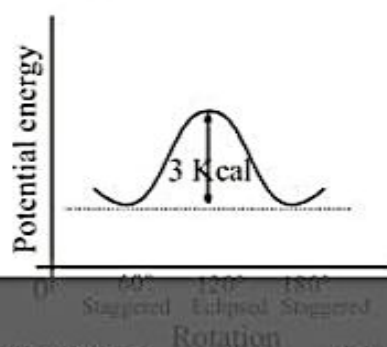
**Stability :** The eclipsed form is less stable than staggered due to Vander Waal repulsion and torsional strain.

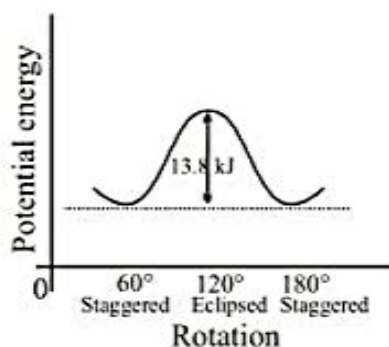
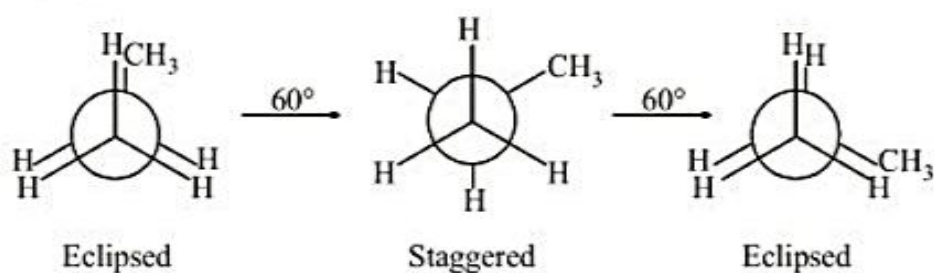


**Vander Waal repulsion :** Repulsion between atoms or group of atoms.

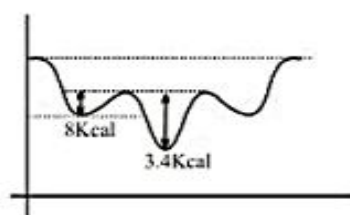
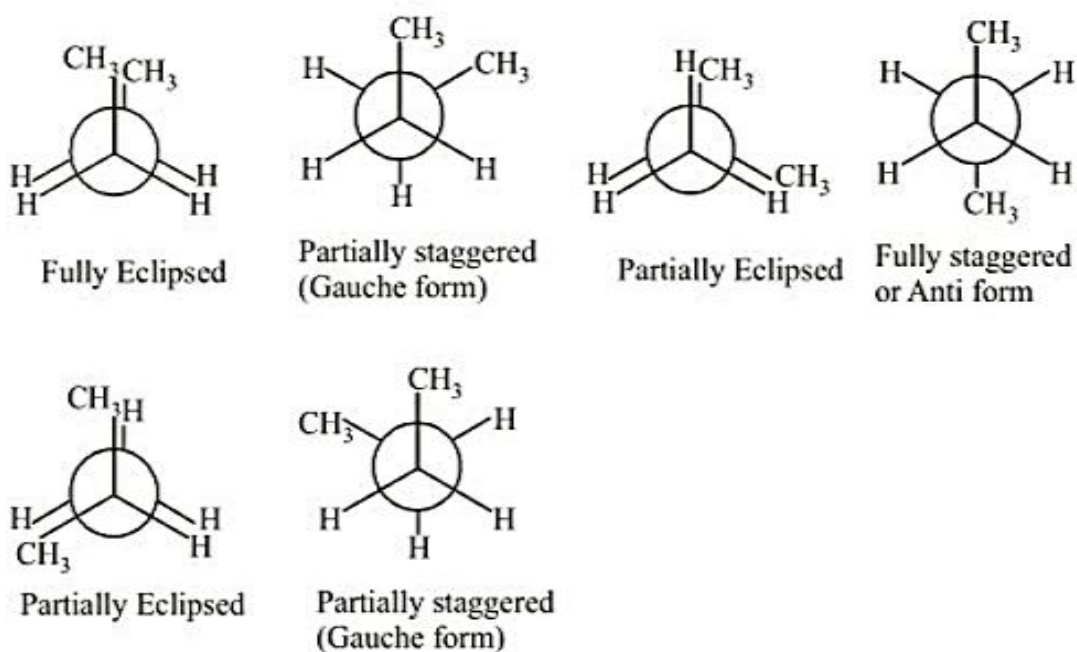
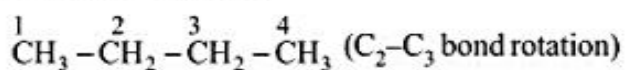
**Torsional strain :** Bond pair-bond pair repulsion in eclipsed form.

**Potential energy curve :**  $E_{\text{ec}} - E_{\text{st}} = 3 \text{ Kcal / mole}$  or  $12.5 \text{ kJ / mole}$



**Conformation in propane :**

$$E_{ec} - E_{st} = 13.8 \text{ kJ/mole}$$

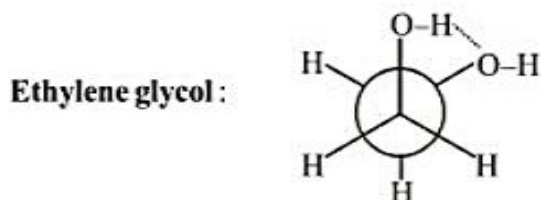
**Conformation in n-butane :**

**Stability order :**      Anti form > Gauche > Partial eclipse > fully eclipsed

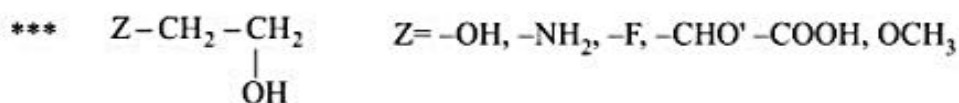


- Exercise :**
- n-pentane (about  $C_2-C_3$ )
  - 3-methyl pentane (about  $C_2-C_3$ )

**Some important example :**

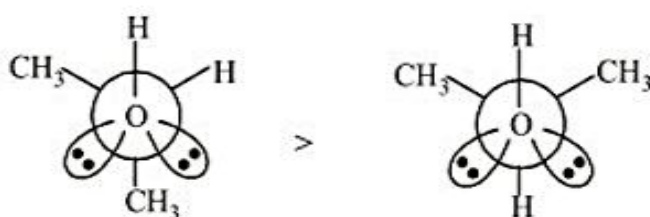
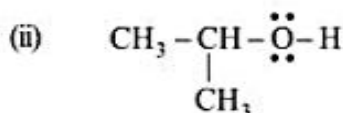
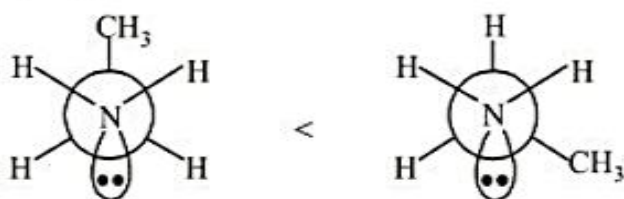


Gauche form is most stable due to intramolecular H-bonding.



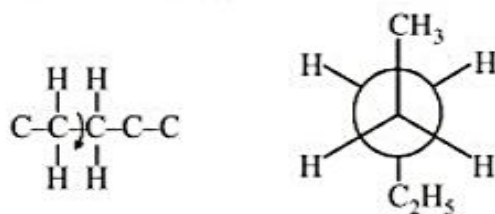
Gauche in all cases due to H-bonding.

**Gauche effect :** In a lone pair containing compound bulkier group should be placed in Gauche ( $60^\circ$ ) from l.p. As l.p. has minimum steric repulsion.

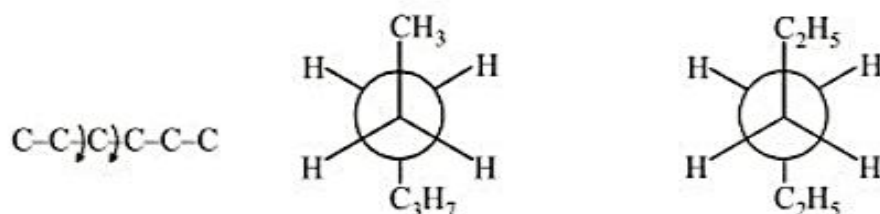


**Draw most stable conformation of following compound.**

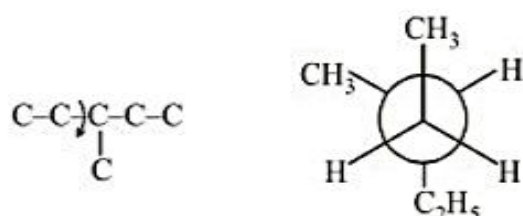
- (i) n-pentane ( $C_2-C_3$ ) bond rotation.



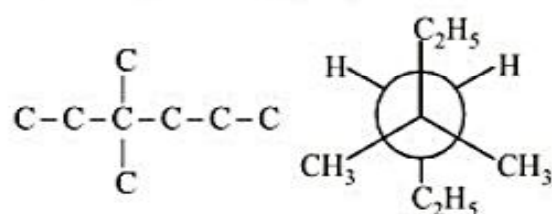
- (ii) n-hexane ( $C_2-C_3$ ) rotation  
( $C_3-C_4$ ) rotation



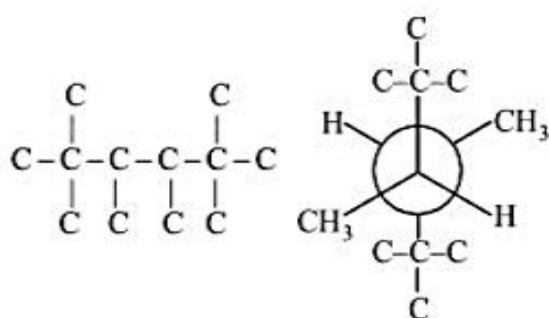
(iii) 3-methyl pentane ( $\text{C}_2-\text{C}_3$ )



(iv) 3,3-dimethyl hexane ( $\text{C}_3-\text{C}_4$ ):

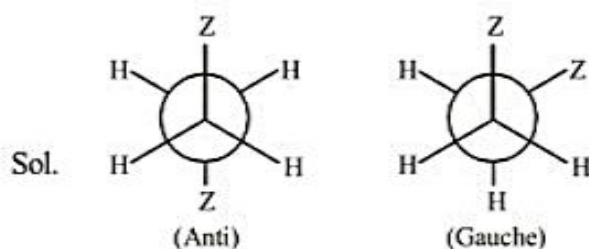


(v) 2,2,3,4,5,5-hexamethyl hexane ( $\text{C}_3-\text{C}_4$ ):



Q. Write stable conformer for  $\text{Z}-\text{CH}_2-\text{CH}_2-\text{Z}$  in Newman's projection. If  $\mu_{\text{solution}} = 1.0 \text{ D}$  and mole fraction of anti form = 0.82, find  $\mu_{\text{Gauche}}$  [JEE 2005]

Ans.  $\mu_{\text{Gauche}} = 5.55 \text{ D}$



Mole fraction of anti form = 0.82

Mole fraction of Gauche form = 0.18

$$\begin{aligned}\mu_{\text{obs.}} &= 1 \\ 1 &= \mu_{\text{(anti)}} \times 0.82 + \mu_{\text{(Gauze)}} \times 0.18 \\ \mu_{\text{(anti)}} &= 0 \\ \therefore 1 &= \mu_{\text{(Gauze)}} \times 0.18 \\ \mu_{\text{Gauze}} &= \frac{1}{0.18} = 5.55 \text{ D}\end{aligned}$$

### Conformation in cyclo alkane :

**Baeyer's strain theory :** According to Baeyer's strain theory, the amount of the strain is directly proportional to the angle through which a valency bond has deviated from its normal position. i.e.

$$\text{Amount of deviation } d = \frac{1}{2} (109^\circ 28' - \text{Valency angle})$$

$$\text{in cyclopropane } d = \frac{1}{2} (109^\circ 28' - 60^\circ) = 24^\circ 44'$$

$$\text{in cyclobutane } d = \frac{1}{2} (109^\circ 28' - 90^\circ) = 9^\circ 44'$$

$$\text{in cyclopentane } d = \frac{1}{2} (109^\circ 28' - 108^\circ) = 0^\circ 44'$$

$$\text{in cyclohexane } d = \frac{1}{2} (109^\circ 28' - 120^\circ) = -5^\circ 16'$$

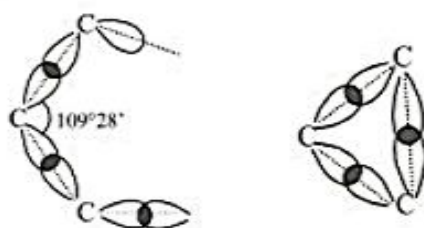
### Heat of combustion :

Cyclohexane > Cyclopentane > Cyclobutane > cyclopropane

### Heat of combustion per $-\text{CH}_2-$

Cyclopropane > Cyclobutane > Cyclopentane > Cyclohexane

### Orbital picture of angle strain :



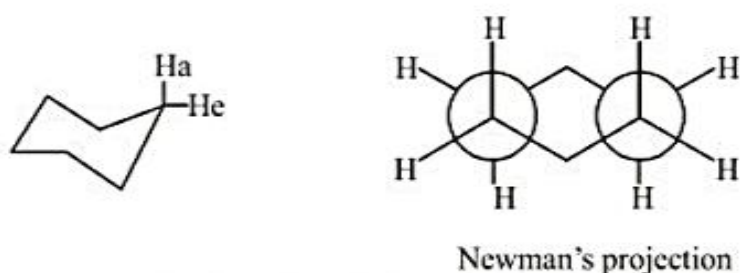
In cyclopropane however, the C-C-C bond angle cannot be  $109^\circ 28'$  but instead must be  $60^\circ$ . As a result the C-atom cannot be located to permit their  $sp^3$  orbitals to point toward each other. there is less overlap and the bond is weaker than the usual C-C bond.

**Conformation of cyclohexane :** Cyclohexane exist in different form, such on chair form, boat form twist boat form, half chair form.

**Stability order :** Chair form > boat form

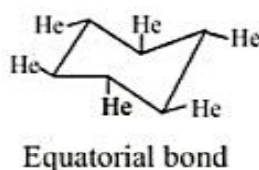
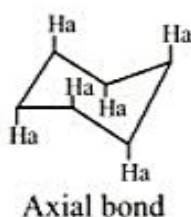
### Boat conformation :



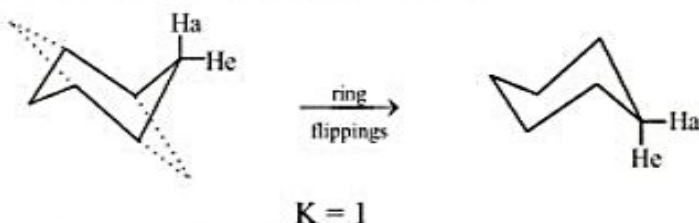
**Chair form of cyclohexane :**

There are two type of hydrogen in cyclohexane:

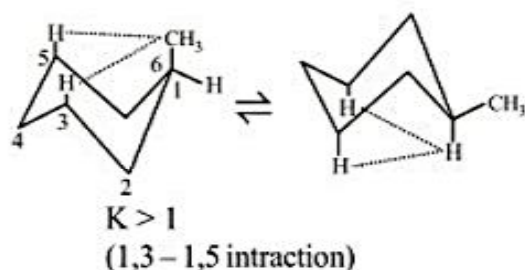
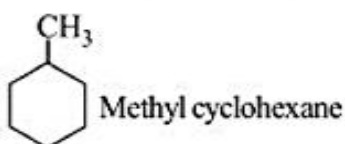
- (i) Axial hydrogen (Ha)
- (ii) Equatorial hydrogen (He)



In cyclohexane all carbon maintain tetrahedral geometry so that cyclohexane is most stable cycloalkane. At room temperature one chair form flips to another chair form during flipping axial bonds converts to equatorial & equatorial bonds converts to axial.



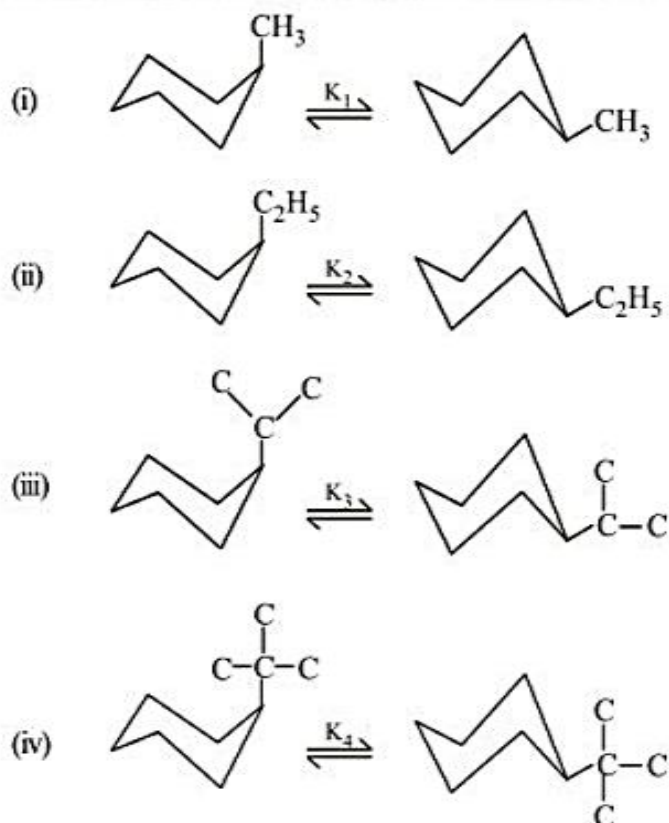
Both chair form are equally stable.

**Conformation of mono substituted cyclohexane :**

When methyl group is add axial position than their will be more 1,3 – 1,5 intraction so that this conformation will be least stable. By ring flipping methyl group occupied equatorial position so that new reverse chair form will be more stable.



Write the orders of equilibrium constant for following equilibrium.



order  $K_1 < K_2 < K_3 < K_4$

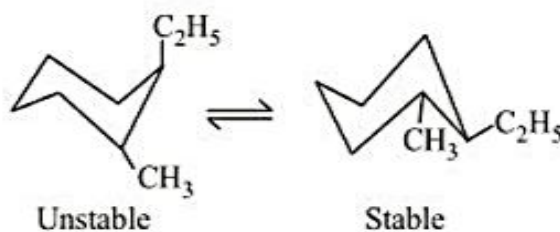
As the size of alkyl group increases 1,3-1,5-interaction also increases, so that bulky alkyl group preferably occupied equatorial position.

Draw most stable chair conformation of following compound.

(a) 1,2-dimethyl cyclohexane



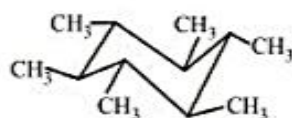
(b) 1-ethyl-2-methyl cyclohexane



(c) 1,3,5-trimethyl cyclohexane



(d) 1,2,3,4,5,6-hexa methyl cyclohexane

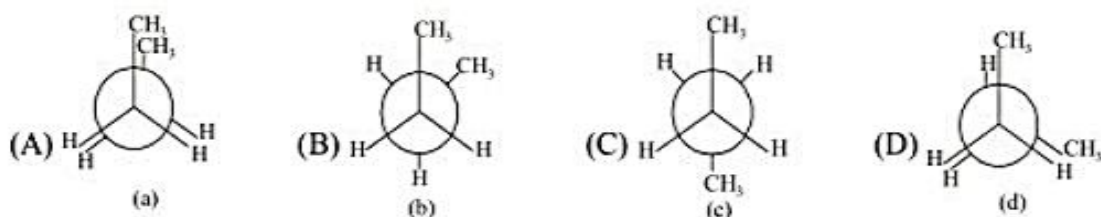


(e) 1-ethyl-2,3-dimethyl cyclohexane

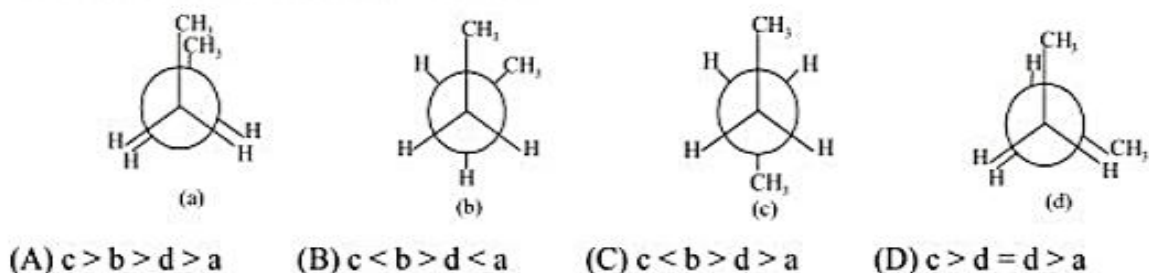


## MCQ

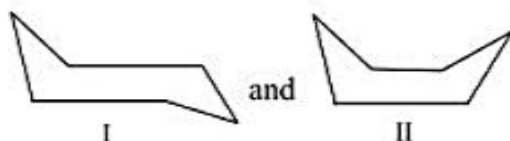
**Q.1** Which form is more stable among all these arrangements



**Q.2** Correct order of stability among the following



**Q.3** Which form is more stable in the shown case-

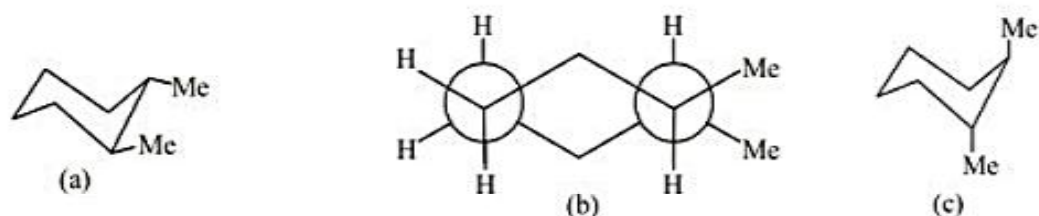


- (A) I      (B) II      (C) I = II      (D) II > I

**Q.4** Increasing order of stability among the three main conformation (i.e. eclipse, anti, gauche) of ethylene glycol is:

- (A) Eclipse, gauche, anti      (B) Gauche, eclipse, anti  
(C) Eclipse, anti, gauche      (D) Anti, gauche, eclipse

**Q.5** The correct stability order of the following species is



- (A)  $c < a < b$       (B)  $c = b < a$       (C)  $c < a = b$       (D)  $a = b = c$

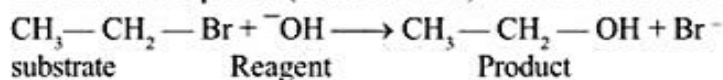
## ANSWERS

- Q.1 C      Q.2 A      Q.3 A      Q.4 C      Q.5 C

## GENERAL ORGANIC CHEMISTRY

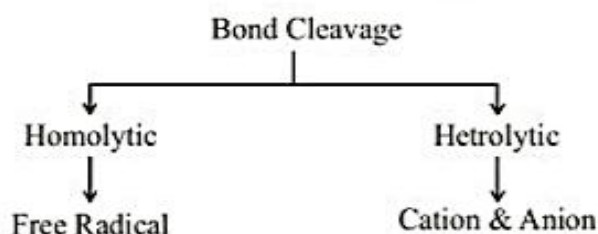
### BOND CLEAVAGE

- Organic reaction is a process in which breaking and formation of covalent bonds takes place.
- In organic reaction, the organic compound which is converted into a new compound by breaking and formation of covalent bonds is known as the **reactant** or **substrate** and the new compound formed is known as the **product**.
- The chemical species (more reactive) which causes the change is called **reagent**.



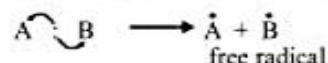
or  
Reactant

Breaking of covalent bond is known as **bond cleavage**. A bond can be broken by two ways :



#### Homolytic Fission or Homolysis

- The covalent bond is broken in such a way that each resulting species gets its own electron. This leads to the formation of odd electron species known as **free radical**.
- Homolytic bond fission gives free radical as the reaction intermediate.



- The factor which favours homolysis is zero or a small difference in electronegativity between A and B.
- Homolytic bond fission takes place in gaseous phase or in the presence of non polar solvents (CCl<sub>4</sub>, CS<sub>2</sub>).

#### Heterolytic Bond Fission or Heterolysis

- In heterolysis, the covalent bond is broken in such a way that one species (i.e., less electronegative) loss its own electron, while the other species (i.e., more electronegative) gains both the electrons.



- Thus formation of opposite charged species takes place. In case of organic compounds, if positive charged is present on the carbon then cation is termed as **carbocation**. If negative charge is present on the carbon then anion is termed as **carbanion**.
- The factor which favours heterolysis is a greater difference of electronegativity between A and B.

### REACTION INTERMEDIATES

Reaction intermediates are generated by the breaking of covalent bond of the substance. They are short-lived species (half life  $\geq 10^{-6}$  sec.) and are highly reactive. few important types of reaction-intermediates are as follows.

- (1) Carbocation      (2) Carbanion      (3) Free radical



## Carbocations

An organic species which has a carbon atom bearing six electrons in its outermost shell and has a positive charge is called a carbocation.

### Characteristics of Carbocation :

- (i) Carbocation have a positive charge on carbon.
- (ii) Positively charged carbocation has only 6 electrons in the outermost shell. It has an incomplete octet. So it behaves like a lewis acid.
- (iii) Since all electrons are in paired state so carbocations are diamagnetic.
- (iv) Carbocations are  $sp^2$  hybridised.
- (v) Carbocations are planar with a perpendicular empty p-orbital. Due to planar structure carbocation leads racemization in stereogenic conditions.
- (vi) Carbocations are formed in polar solvent.
- (vii) It stabilize by presence of electron donating group (EDG)

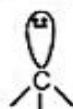
## Carbanions

Anion of carbon is known as carbanion. Carbanion carries three bond pairs and one lone pair, thus making the carbon atom negatively charged thus carbanion may be represented as



### Characteristic of Carbanions :

- (i) It is formed by heterolytic bond fission.
- (ii) There are eight electrons in the outermost orbit of carbanionic carbon hence its octet is complete.
- (iii) It behaves as charged nucleophile.
- (iv) It is diamagnetic in character because all eight electrons are paired.
- (v) Hybridisation and geometry : Alkyl carbanion has three bond pairs and one lone pair. Thus hybridisation is  $sp^3$  and geometry is pyramidal.



**Note :** Geometry of allyl and benzyl cabanion is almost planar and hybridisation is  $sp^2$ .

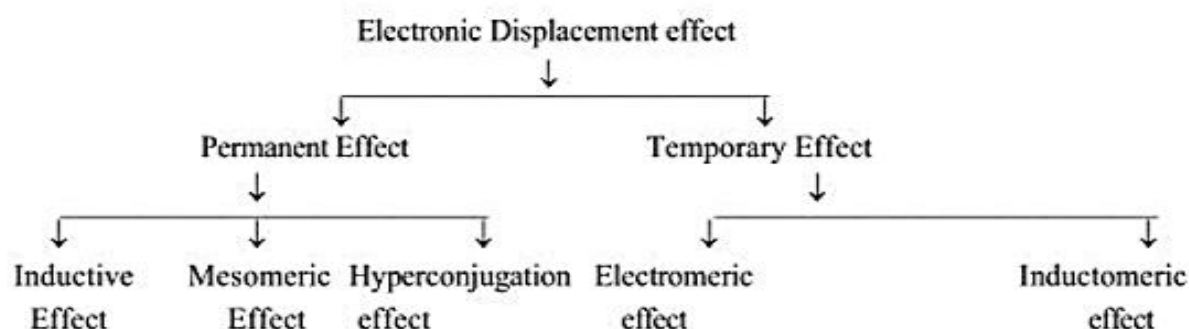
- (vi) It reacts with electrophiles.
- (vii) It stabilize by presence of electron withdrawing group (EWG)

## Carbon Free Radical

- (i) Carbon free radicals are odd electron species in which carbon atom bears the odd electron.
- (ii) Homolytic bond fission of a covalent single bond gives rise to free radicals.
- (iii) There are seven electrons in the outer most shell of carbon free radicals.
- (iv) Owing to the presence of an odd electron; a carbon radical is paramagnetic in nature. Due to this reason free radicals are highly reactive.
- (v) Carbon free radicals are normally  $sp^2$  hybridized
- (vi) Free radicals are neutral electrophiles.
- (vii) It stabilize by presence of electron releasing group (ERG)

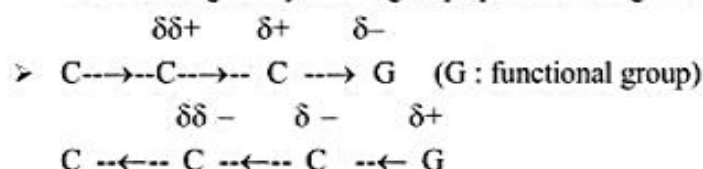


## ELECTRONIC DISPLACEMENT EFFECTS (EDE)



## INDUCTIVE EFFECT (I-EFFECT)

The displacement (shifting) of an electron (shared) pair along the carbon chain due to the difference in electronegativity of the groups present along with carbon chain is known as inductive effect.



But the effect is insignificant beyond third carbon atom. (distance dependent effect)

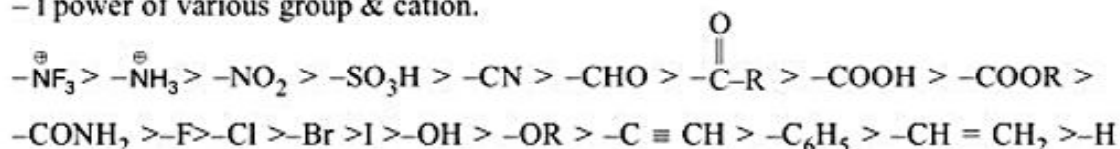
- This effect is transmitted through the chain of  $\sigma$  bonds and diminishes, with increasing chain length. Inductive effect is thus

- (i) A permanent effect
- (ii) The electrons never leave their original atomic orbital.
- (iii) Operates through  $\sigma$  bonds
- (iv) Polarisation of electrons is always in single direction.
- (v) It is generally observed in saturated compounds.
- (vi) Its magnitude (i.e., electron withdrawing or donating power) decreases with increase in distance.

On the basis of electron realising group (ERG) or electron withdrawing group (EWG) inductive effect, can be of two types.

– *I* effect : The group which withdraws electrons is known as – *I* group and its effect is known as – *I* effect.

– *I* power of various group & cation.

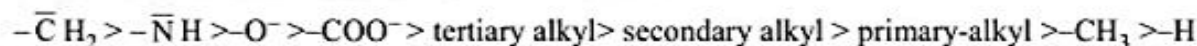


– *I* power of groups in decreasing order with respect to the reference H

+ *I* effect : The group which donates or gives electron is known as + *I* group and effect is known as + *I* effect.

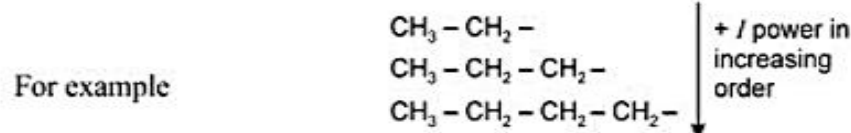
e.g., Alkyl groups,  $-\overset{\ominus}{\text{O}}-$ ,  $-\overset{\ominus}{\text{C}}-\overset{\ominus}{\text{O}}-$  are + *I* groups. (Generally negative charged atoms or groups)

## (a) +I power of different type groups and anions :



+I power in decreasing order with reference to H-atom

## (b) +I power of same type of alkyl groups :

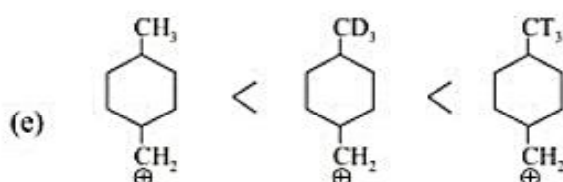
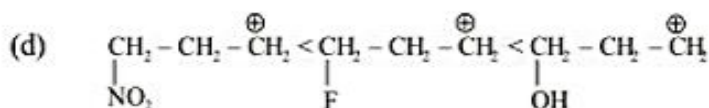
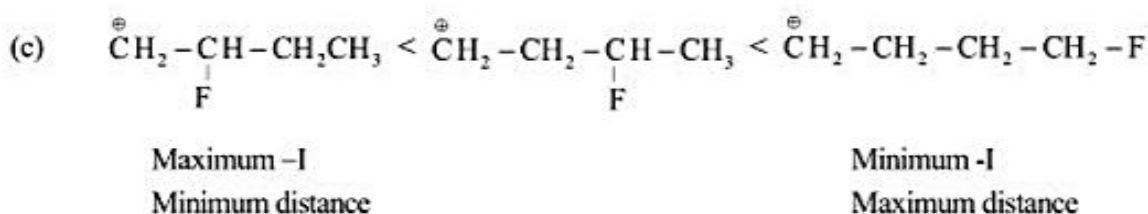
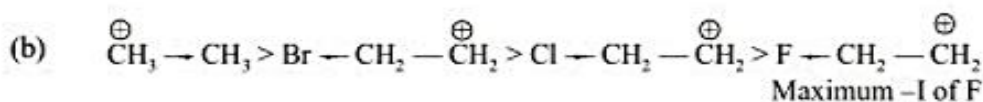
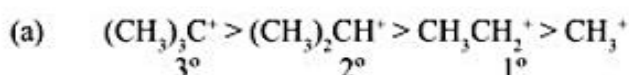
+I power  $\propto$  number of C's in same type of alkyl group

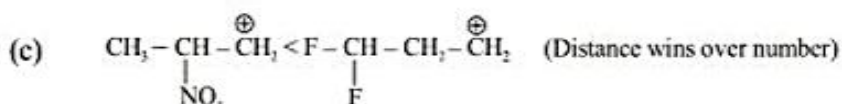
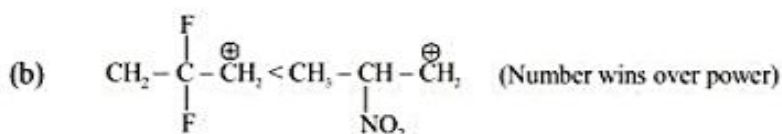
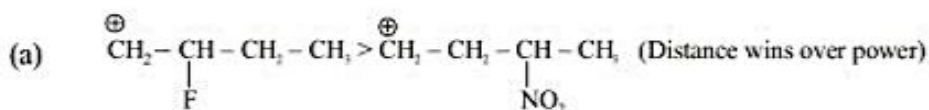
## APPLICATIONS OF INDUCTIVE EFFECT

## (A) Stability of reaction intermediates

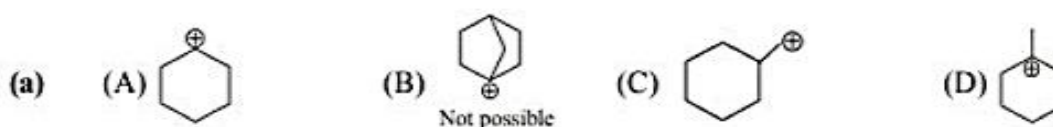
(i) Stability of carbocation (ii) Stability of free Radical (iii) Stability of carbanion

## (i) Stability of carbocation

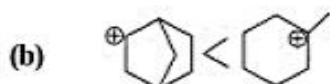
Stability of carbocation  $\propto$  Presence of electron releasing group  $\propto$  +I group  $\propto \frac{1}{-I \text{ group}}$ **Note-1 :** - DNP Rule : - (Distance Number Power Rule)

**Example****Note-2**

**Bredt's Rule** : Formation of carbocation, free radical and  $\pi$ -bond at bridge head position is not possible due to angle strain.

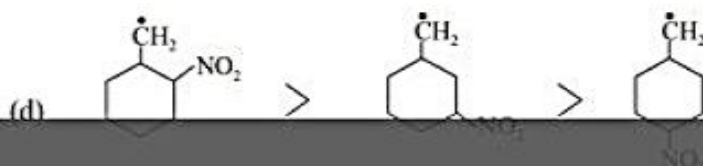
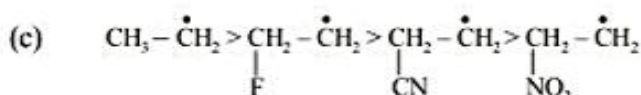
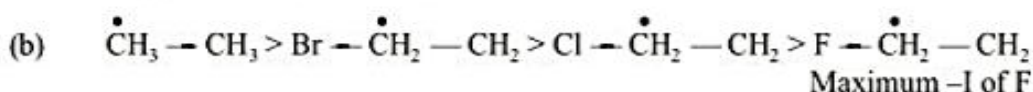
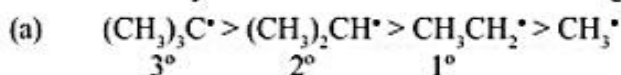
**Examples :-**

Stability order : d > a > c > b

**(ii) Stability of free Radical**

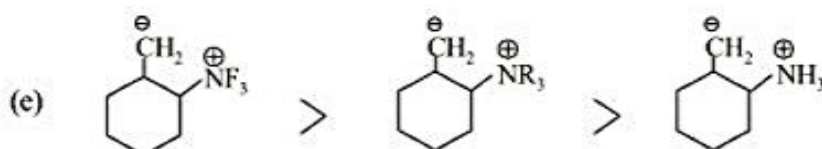
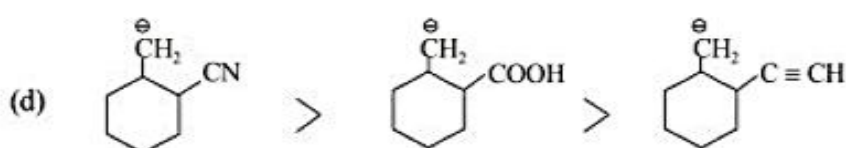
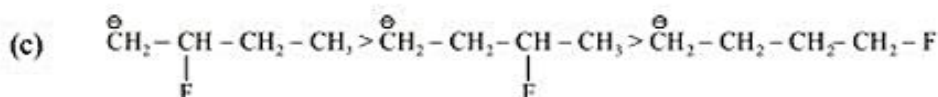
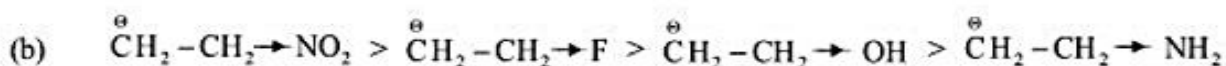
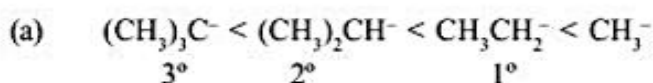
Stability of F.R.  $\propto$  Presence of electron releasing group  $\propto$  +I group  $\propto \frac{1}{-I \text{ group}}$

Stability of F.R. decrease in the following order

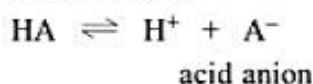


**(iii) Stability of carbanion**

Stability of carbanion  $\propto$  Presence of electron withdrawing group  $\propto -I$  group  $\propto \frac{1}{+I \text{ group}}$ .

**(B) Acidic Strength**

**Strength of Carboxylic Acid :** Acid strength is measured by the position of equilibrium of ionisation in water.



or  $K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$  ( $K_a$  = acid ionisation constant)

or, acid strength  $\propto [\text{H}^+] \propto K_a \propto \frac{1}{\text{p}K_a}$   
 (here  $\text{p}K_a = -\log K_a$ )

or Acid strength  $\propto$  concentration of  $[\text{H}^+]$

or Acid strength  $\propto$  stability of acid anion

**Thus strength of acid is the function of stability of acid anion.**

$\therefore$  Stability of carbanion  $\propto$  Presence of electron withdrawing group  $\propto -I$  group  $\propto \frac{1}{+I \text{ group}}$

$\therefore$  acidic strength  $\propto$  Presence of electron withdrawing group  $\propto -I$  group  $\propto \frac{1}{+I \text{ group}}$

The influence of the inductive effect on acidity can be summarised as follows :



**Acidic strength of carboxylic acid**

- (a)  $\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$
- (b)  $\text{CH}_4 < \text{NH}_4 < \text{H}_2\text{O} < \text{HF}$
- (c)  $\text{Cl}-\text{CH}_2-\text{COOH} < \text{Cl}_2\text{CH}-\text{COOH} < \text{CCl}_3-\text{COOH}$   
            $-I \uparrow$                       acid strength  $\uparrow$
- (d)  $\text{H}-\text{COOH} > \text{CH}_3-\text{COOH} > \text{CH}_3-\text{CH}_2-\text{COOH} > \text{CH}_3-\text{CH}_2-\text{CH}_2-\text{COOH}$   
            $+I$  power of alkyl groups  $\uparrow$                       Acid strength  $\downarrow$
- (e)  $\begin{array}{c} \text{CH}_2-\text{OH} \\ | \\ \text{Cl} \end{array} > \begin{array}{c} \text{CH}_2-\text{CH}_2-\text{OH} \\ | \\ \text{NO}_2 \end{array}$   
           I                      II
- (f)  $(\text{CH}_3)_3\text{COH} < (\text{CH}_3)_2\text{CHOH} < \text{CH}_3\text{CH}_2\text{OH} < \text{CH}_3\text{OH}$

**(C) Basic Strength****Basicity of Amines :**

Basicity is defined as the tendency to donate an electron pair for sharing. The difference in the base strength in various amines can be explained on the basis of  $+I$  - effect.

The groups producing  $+I$  effects (alkyl groups) tends to intensify electron density over N in amines thereby producing a base strengthening effect.

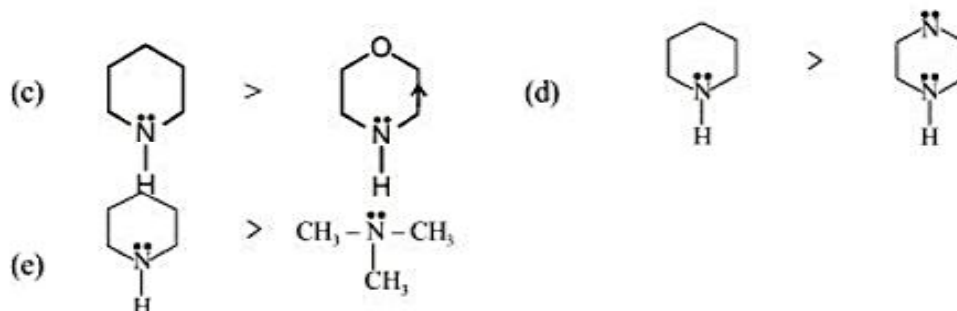
Thus, strength of base  $\propto +I$  power of group present on  $-\text{NH}_2 \propto K_b \propto \frac{1}{pK_b}$

Whereas, a group producing  $-I$  effect  $[-\text{Cl}, -\text{NO}_2]$  tends to decrease electron density over N - atom in amines, thereby producing a base weakening effect.

Thus, strength of base  $\propto \frac{1}{-I \text{ power of group present on } -\text{NH}_2} \propto K_b$

**Relative base strength of amines :****Examples**

- (a)  $\text{R}-\text{NH}_2 < \text{R}_2\text{NH} < \text{R}_3\text{N}$                       (b)  $\text{H}_2\text{O} < \text{NH}_3 < \text{NH}_2^-$

**Order of basic strength in solvent phase**

- (f)  $\text{R} = \text{CH}_3 \rightarrow \text{R}_2\text{NH} > \text{RNH}_2 > \text{R}_3\text{N} > \text{NH}_3$
- (g)  $\text{R} = \text{C}_2\text{H}_5 \rightarrow \text{R}_2\text{NH} > \text{R}_3\text{N} > \text{RNH}_2 > \text{NH}_3$

## MCQ

- Q.1 Homolytic fission of organic compound yields-  
 (A) Nucleophile (B) Carbanion (C) Free radical (D) Carbocation
- Q.2 The number of electrons present in the valence shell of carbon of  $\text{CH}_3\dot{\text{C}}\text{H}_2$  ion bearing +ve charge:  
 (A) 8 (B) 7 (C) 6 (D) 4
- Q.3 Inductive effect refers to -  
 (A)  $\sigma$  electron displacement along a carbon chain  
 (B) complete transfer of one of the shared pair of electrons to one of the atoms joined by a double bond  
 (C) complete transfer of electron with the help of conjugation  
 (D) none of the above
- Q.4 Most acidic hydrogen is present in-  
 (A) Ethyne (B) Ethene (C) Benzene (D) Ethane
- Q.5 The least acidic among the following acids is-  
 (A) Trichloroacetic acid (B) Dichloroacetic acid  
 (C) Monochloroacetic acid (D) Acetic acid.
- Q.6 Among the following which one is most basic-  
 (A)  $\text{NH}_3$  (B)  $\text{CH}_3\text{NH}_2$  (C)  $\text{CH}_3\text{CH}_2\text{NH}_2$  (D)  $\begin{array}{c} \text{CH}_2\text{-NH}_2 \\ | \\ \text{Cl} \end{array}$
- Q.7 Which one is the characteristic feature of a free radical :  
 (A) presence of positive charge (B) presence of unpaired electron  
 (C) presence of even number of electrons (D) associated with high stability
- Q.8 Benzoylperoxide, when heated to about  $80^\circ\text{C}$  gives a-  
 (A) Free radical (B) Carbanion (C) Carbocation (D) None of these
- Q.9 Which one is a  $1^\circ$  carbocation of the following:  
 (A)  $\text{CH}_3\dot{\text{C}}\text{H}_2$  (B)  $\text{CH}_3\dot{\text{C}}\text{H}-\text{C}_2\text{H}_5$  (C)  $(\text{CH}_3)_2\dot{\text{C}}\text{H}$  (D)  $(\text{CH}_3)_3\dot{\text{C}}$
- Q.10  $\text{CH}_3^\ominus$  is less stable than  
 (A)  $\text{CH}_3-\text{CH}_2^\ominus$  (B)  $\text{CH}_3-\text{CH}^\ominus-\text{CH}_3$  (C)  $\text{CH}_2^\ominus-\text{NO}_2$  (D)  $\text{CH}_3-\text{CH}^\ominus-\text{C}_2\text{H}_5$
- Q.11 Which of the following groups has the highest +I effect?  
 (A)  $-\text{CH}_3$  (B)  $\text{CH}_3-\text{CH}_2-$  (C)  $(\text{CH}_3)_2\text{CH}-$  (D)  $(\text{CH}_3)_3\text{C}-$

Q.12 Decreasing order of -I effect of the triad  $\left[ -\text{NO}_2, \overset{\oplus}{\text{N}}\text{H}_3, -\text{CN} \right]$  is

- (A)  $-\overset{\oplus}{\text{N}}\text{H}_3 > -\text{NO}_2 > -\text{CN}$  (B)  $-\overset{\oplus}{\text{N}}\text{H}_3 > -\text{CN} > -\text{NO}_2$   
 (C)  $-\text{CN} > -\text{NO}_2 > \overset{\oplus}{\text{N}}\text{H}_3$  (D)  $-\text{NO}_2 > -\text{CN} > \overset{\oplus}{\text{N}}\text{H}_3$

Q.13 Maximum -I effect is exerted by the group-

- (A)  $-\text{C}_6\text{H}_5$  (B)  $-\text{OCH}_3$  (C)  $-\text{Cl}$  (D)  $-\text{NO}_2$

Q.14 Choose the strong base from each of the following pair

- (1)  $^-\text{OC}_2\text{H}_5, ^-\text{OH}$  (2)  $\text{HC} \equiv \text{C}^-, \text{CH}_3^-$  (3)  $\text{Br}^-, \text{I}^-$  (4)  $\text{CH}_3^-, \text{NH}_2^-$   
 (1) (2) (3) (4)  
 (A)  $^-\text{OC}_2\text{H}_5, \text{CH}_3^-, \text{Br}^-, \text{CH}_3^-$   
 (B)  $\text{OH}^-, \text{CH}_3^-, \text{I}^-, \text{NH}_2^-$   
 (C)  $\text{OH}^-, \text{HC} \equiv \text{C}^-, \text{Br}^-, \text{CH}_3^-$   
 (D)  $\text{OH}^-, \text{CH}_3^-, \text{I}^-, \text{NH}_2^-$

Q.15 Basic nature of  $\text{H}_3\text{O}^+, \text{H}_2\text{O}$  and  $\text{OH}^-$  is in order -

- (A)  $\text{H}_3\text{O}^+ < \text{H}_2\text{O} < \text{OH}^-$  (B)  $\text{H}_2\text{O} < \text{OH}^- < \text{H}_3\text{O}^+$   
 (C)  $\text{OH}^- < \text{H}_2\text{O} < \text{H}_3\text{O}^+$  (D)  $\text{OH}^- = \text{H}_3\text{O}^+ = \text{H}_2\text{O}$

Q.16 Which is most stable carbocation

- (A)  $\text{CH}_3\text{CH}_2^+$  (B)  $\text{CH}_3^+$  (C)  $\text{CH}_3-\overset{+}{\text{C}}\text{H}-\text{CH}_3$  (D)  $\text{CH}_3\text{CH}_2-\overset{+}{\text{C}}\text{H}_2$

Q.17 Among the following compounds, the weakest acid is-

- (A)  $\text{HC} \equiv \text{CH}$  (B)  $\text{C}_6\text{H}_6$  (C)  $\text{C}_2\text{H}_6$  (D)  $\text{CH}_3\text{OH}$

Q.18 Most stable carbanion is

- (A)  $\text{HC} \equiv \text{C}^-$  (B)  $\text{C}_6\text{H}_5^-$  (C)  $(\text{CH}_3)_3\text{C}-\text{CH}_2^-$  (D)  $(\text{CH}_3)_2\text{C}=\text{CH}^-$

Q.19 Which of the following compounds is most acidic?

- (A)  $\text{CH}_3\text{COOH}$  (B)  $\text{CH}_3\text{CH}_2\text{OH}$  (C)  $\text{CH}_2\text{ClCOOH}$  (D)  $\text{CCl}_3\text{COOH}$

Q.20 Which is the decreasing order of stability

- (a)  $\text{CH}_3-\overset{+}{\text{C}}\text{H}-\text{CH}_3$  (b)  $\text{CH}_3-\overset{+}{\text{C}}\text{H}-\text{O}-\text{CH}_3$  (c)  $\text{CH}_3-\overset{+}{\text{C}}\text{H}-\text{CO}-\text{CH}_3$   
 (A)  $a > c > b$  (B)  $a > b > c$  (C)  $c > b > a$  (D)  $b > a > c$

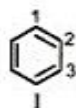


## ANSWERS

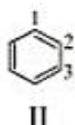
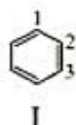
Q.1	C	Q.2	C	Q.3	A	Q.4	A	Q.5	D	Q.6	C
Q.7	B	Q.8	A	Q.9	A	Q.10	C	Q.11	D	Q.12	A
Q.13	D	Q.14	A	Q.15	A	Q.16	C	Q.17	C	Q.18	A
Q.19	D	Q.20	D								

## RESONANCE

Consider structures of benzene :



According to the given structure  $C_1-C_2$  bond length should be smaller than  $C_2-C_3$  bond length but  $C_1-C_2$  and  $C_2-C_3$  bond length must be equal. So this bond length data is not explained by single structure so we need two structures of benzene which is following



I and II are resonating structures of  $C_6H_6$ .

When a molecule or ion can not be represented by single lewis dot structure and more than one structure are needed to represent all properties of the molecule these structures are known as resonating structure and combined structure of all resonating structure are known as resonance hybrid and this phenomenon is known as resonance.

- Resonating structure have the same arrangement of atomic nuclei but differ in distribution of electrons, (only  $\pi$  electron delocalised)
- Resonating structure are hypothetical and actual structure is a resonance hybrid.
- Resonance generally occurs when there is a conjugation of  $\pi$ -bonds (alternate double - single - double bond arrangement)

## Condition for Resonance :

- Planarity - Atoms considered in molecules must be  $sp^2$  or  $sp$ -hybridised not  $sp^3$  hybridised.
- Conjugation - System in which p-orbitals are arranged parallel and continuous to each other is considered as conjugated system.

- Negative charge alternate to  $\pi$  electron conjugation
- Lone pair electron alternate to  $\pi$  electron conjugation
- $\pi$  electron alternate to  $\pi$  electron conjugation
- $\pi$  electron alternate to vacant orbital (Positive charge) conjugation
- $\pi$  electron alternate to odd electron (free radical) conjugation
- Lone pair electron alternate to vacant orbital (Positive charge) conjugation

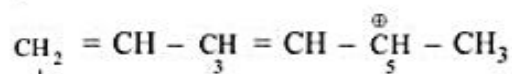
## Conjugate positions of the molecule :

Alternate positions of the molecule having  $\pi$  bond, positive charge, negative charge, odd electron or lone pair of electrons are known as conjugative positions.

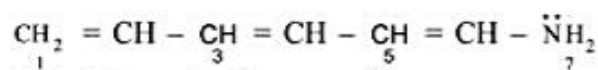




1, 3, 5 are alternate positions having  $\pi$  bonds. Hence these positions are known as conjugate positions.



1, 3 and 5 are conjugate positions.

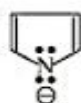
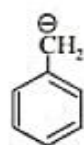
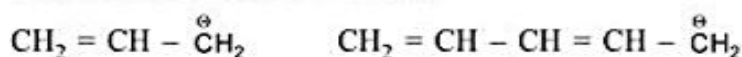


1, 3, 5, 7 are Conjugate positions

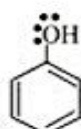
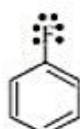
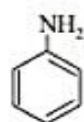
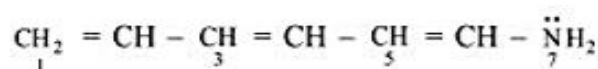
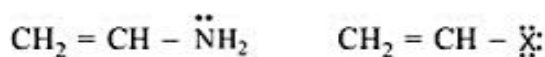
**Note :** Compound having at least two conjugate positions is known as conjugated compound.

## TYPES OF CONJUGATIONS

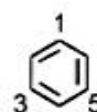
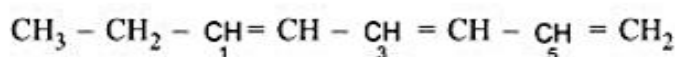
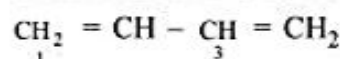
- (1) **Negative charge electron alternate to  $\pi$  electron conjugation :** If in a conjugated system  $\pi$  bond and  $\ominus$  charge at alternate position so conjugation is known as negative charge electron alternate to  $\pi$  electron conjugation



- (2) **Lone pair electron alternate to  $\pi$  electron conjugation :** If in a conjugated system  $\pi$  bond and lone pair at alternate position so conjugation is known as lone pair electron alternate to  $\pi$  electron conjugation.

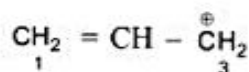


- (3)  **$\pi$  electron alternate to  $\pi$  electron conjugation :** If  $\pi$  bond alternate with  $\pi$  bond so conjugation is known as  $\pi$  electron alternate to  $\pi$  electron conjugation

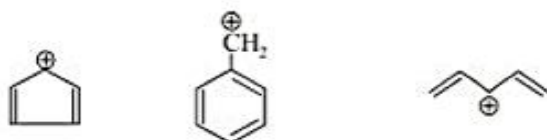
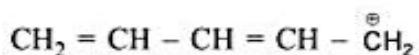


All of the above compounds have  $\pi - \pi$  conjugation.

- (4)  **$\pi$  electron alternate to vacant orbital (Positive charge) conjugation** : If  $\pi$  bond alternate with vacant orbital so conjugation is known as positive charge alternate to  $\pi$  electron conjugation.

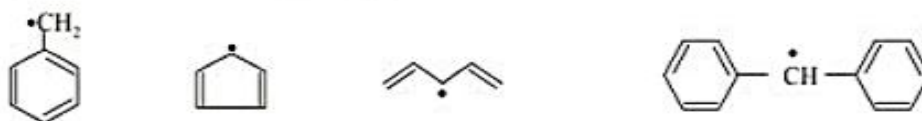
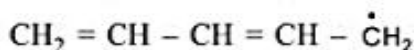
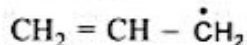


It has positive charge,  $\pi$  conjugation.

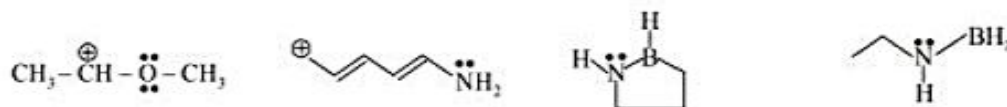
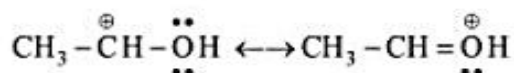
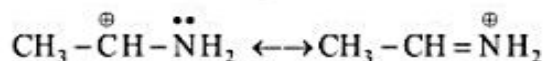


These species has two type of conjugation  $\pi$  electron alternate to  $\pi$  electron conjugation and positive charge alterante to  $\pi$  electron conjugation.

- (5)  **$\pi$  electron alternate to odd electron (free radical) conjugation** : If  $\pi$  bond and odd  $e^-$  are in alternate position.

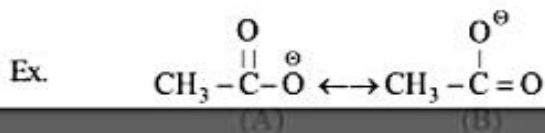


- (6) **Lone pair electron alternate to vacant orbital (Positive charge) conjugation** : If lone pair and vacant orbital are alternate position

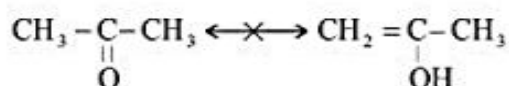


### Rules to draw valid resonating structures

1. Electron flow occurs from high electron density to low electron density.  
Negative charge  $\rightarrow$  Lone pair electron  $\rightarrow$   $\pi$ -bond electron  $\rightarrow$   $\delta^+$   $\rightarrow$  positive charge
2. Position of atom cannot be change, only the  $\pi$ -electrons are delocalised.

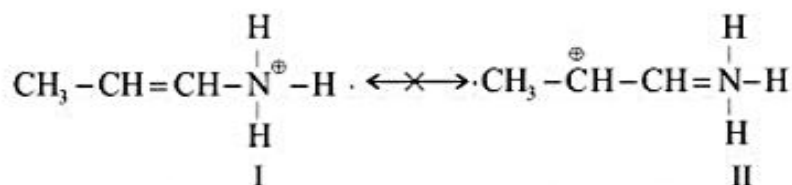


A & B are Resonance forms.



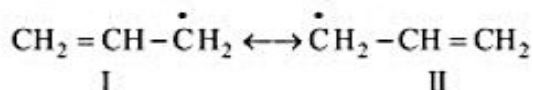
Above forms are not resonating forms because position of H is changed.

3. Second period elements should not violate the octet rule while drawing resonating structures



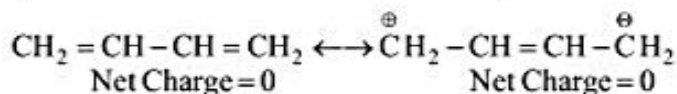
Above structures are not resonance form because in structure II, nitrogen has 10 valence electrons which violates octet rule.

4. Each Resonating structures must have the same number of unpaired and paired electrons.



I & II are resonating structure because both have 8 paired electrons and 1 unpaired electron

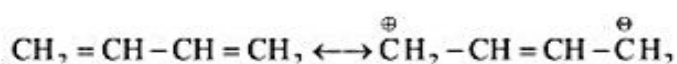
5. Net charge should be conserved in all resonating structures.



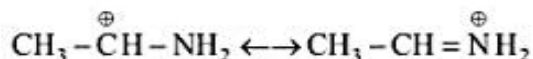
Both structures have same net charge so both are resonance forms.

#### Rules for stability of resonating structures

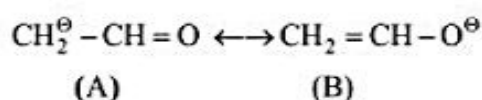
1. Among various resonating structure non polar resonating structure is more stable than polar resonating structure more number of covalent bonds is considered to be more contributing than others.



2. If two resonance structures have same number of bonds then that structure in which octet of every atom is complete is more contributing than structure having incomplete octet.



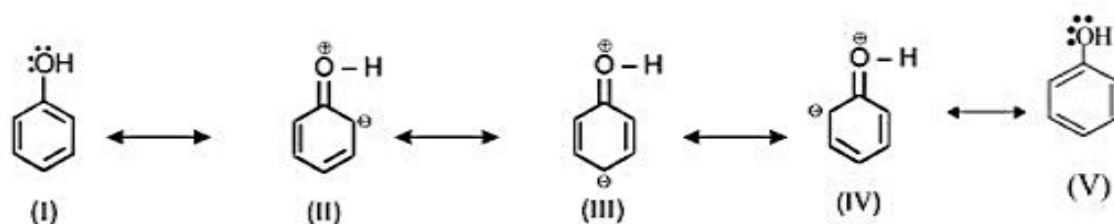
3. If resonating structures have same number of bonds then the neutral structure is more stable than charged structure and if both are charged Resonating structure then less charged resonating structure is more stable.
4. In case of charged resonating structures, the most stable one is that in which the positive and negative charge reside on the most electropositive and most electronegative atoms of the structure respectively.



stability of B > A

5. Resonating structure in which unlike charges are closer is more contributing than that structures in which unlike charges are far away.





Hence stability of II and IV will be the same and both will be more stable than III. The order of stability of resonating structures in decreasing order will be as follows :

$$I = V > II \equiv IV > III$$

6. Resonating structure in which like charges are farer away is more contributing as compared to structure in which like charges are closer.

## RESONANCE ENERGY

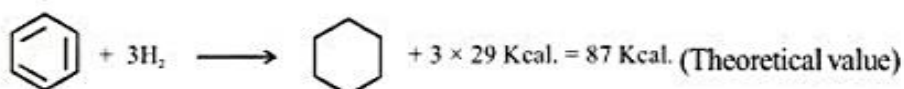
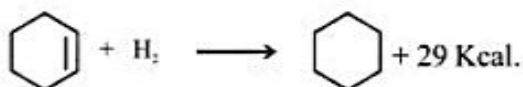
The energy difference between most stable resonating structure and resonance hybrid is known as resonance energy.

- It's the experimental value which is calculated by heat of hydrogenation (HOH)
- Higher the value of resonance energy, greater is the resonance stabilization.

### Resonance Energy of Benzene :



The resonance energy of benzene is calculated from the heat of hydrogenation as given below :

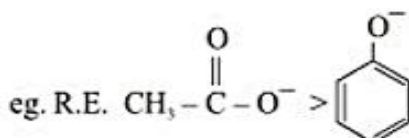


but experimental value for benzene is 51 Kcal. so,

$$\begin{aligned} \text{Resonance energy} &= \text{Calculated value} - \text{Experimental value} \\ &= 87 - 51 \\ &= 36 \text{ Kcal.} \end{aligned}$$

### Resonance energy comparison

1. Consider better resonance or equivalent resonating structures, molecules having equivalent resonating structures must have more resonance energy, than non-equivalent resonating structures.

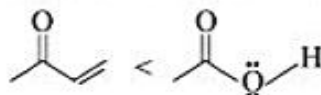


2. Aromatic compound have more resonance energy than non-aromatic compound.



3. In case of larger conjugation, more will be the Resonance energy.

4. Resonance energy will be more, when  $\pi$ -bond, lone pair conjugation is present than  $\pi, \pi$ -conjugation




### MCQ

Q.1 Which molecule does not show resonance

- (A) CO (B) CO<sub>2</sub> (C) CO<sub>3</sub><sup>-2</sup> (D) NO<sub>3</sub><sup>-</sup>

Q.2 Polarization of electrons in acrolein may be written as -

- (A)  $\overset{\delta^+}{\text{CH}_2} = \text{CH} - \text{CH} = \overset{\delta}{\text{O}}$  (B)  $\overset{\delta^+}{\text{CH}_2} = \text{CH} - \overset{\delta^-}{\text{CH}} = \text{O}$   
 (C)  $\overset{\delta^-}{\text{CH}_2} = \overset{\delta^+}{\text{CH}} - \text{CH} = \text{O}$  (D)  $\overset{\delta^-}{\text{CH}_2} = \text{CH} - \text{CH} = \overset{\delta^+}{\text{O}}$

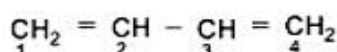
Q.3 In pyridine ;  Number of conjugated electrons are -

- (A) 6 (B) 8 (C) zero (D) 5

Q.4 In which compound delocalization is not possible -

- (A) 2-butene (B) 1, 3-butadiene (C) 1, 3, 5-hexatriene (D) Benzene

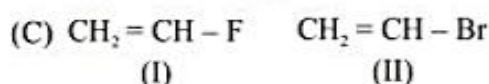
Q.5 Consider the following compound :



carbon-carbon bond length between C<sub>2</sub> and C<sub>3</sub> will be -

- (A) 1.54 Å (B) 1.3 Å  
 (C) 1.21 Å (D) Less than 1.54 and greater than 1.33 Å

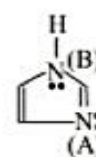
Q.6 Which compound has higher resonance energy in the following pairs



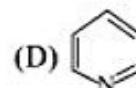
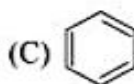
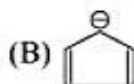
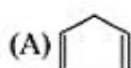
Q.7 Which is less stable canonical structure in the following pairs



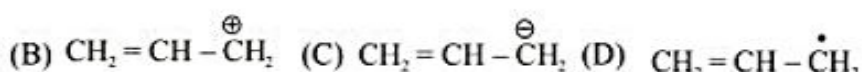
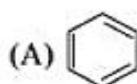
Q.8 Which marked atom's lone pair participate in resonance phenomenon



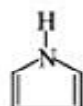
Q.9 Which molecules is not showing resonance



Q.10 Which molecules is showing  $\pi$ -electron alternate to  $\pi$ -electron conjugation

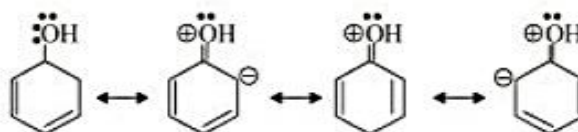


Q.11 Correct order for resonance energy in the following molecules



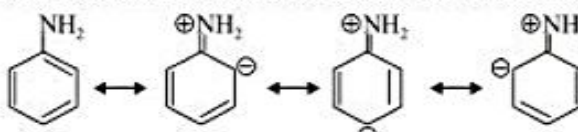
- (A)  $\text{III} > \text{I} > \text{II}$  (B)  $\text{III} = \text{I} = \text{II}$  (C)  $\text{III} < \text{I} < \text{II}$  (D)  $\text{III} = \text{I} > \text{II}$

Q.12 In the following canonical structures which is most stable structure



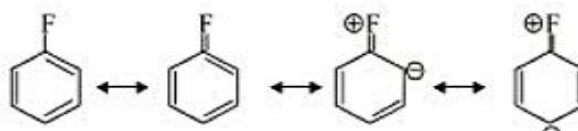
- (A) I (B) II (C) III (D) IV

Q.13 In the following canonical structures which is least stable structure



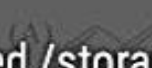
- (A) I (B) II (C) III (D) IV

Q.14 Which is incorrect canonical structure

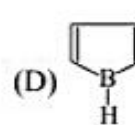
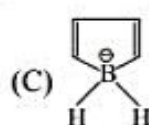
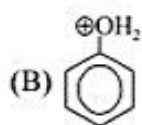
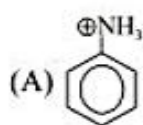


- (A) I (B) II (C) III (D) IV

Q.15 In which molecules non-conjugation is present



Q.16 In which molecule resonance phenomenon operates-

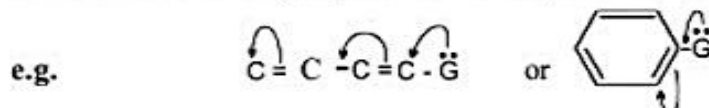


### ANSWERS

Q.1 A	Q.2 A	Q.3 A	Q.4 A	Q.5 D	Q.6 (A) II, (B) II, (C) I
Q.7 (A) II	Q.8 (B)	Q.9 A	Q.10 A	Q.11 A	Q.12 A
Q.13 C	Q.14 B	Q.15 C	Q.16 D		

### MESOMERIC EFFECT

- This is a permanent effect where the displacement of conjugational  $\pi$  electrons are influenced by the group attached to carbon chain.
- There is a push or pull of  $\pi$  electrons of the conjugated system of molecule.
- M effect operates only in the conjugated system.
- If the conjugation is not available, M effect does not propagate further.
- M-effect has no correlation with the electronegativity of the connecting atom of the group
- M-effect is two type; +M and -M
- +M effect (+R) :** If the group pushes the electrons into the  $\pi$  electron system, the effect is said as +M effect and the group is called ERG (electron releasing group) or +M group.



+ M Effect is shown by :  $-\text{Cl}$ ,  $-\text{Br}$ ,  $-\text{NH}_2$ ,  $-\text{NHR}$ ,  $-\text{NR}_2$ ,  $-\text{NHCOCH}_3$ ,  $-\text{OH}$ ,  $-\text{OR}$

**Condition :** Electron pair must be present at first atom of group.

- M effect (-R) :** If the  $\pi$  electrons are present system is pulled by the group then the effect is called -M effect and the group is called EWG group (electron withdrawing group) or -M group.



-M effect is shown by :

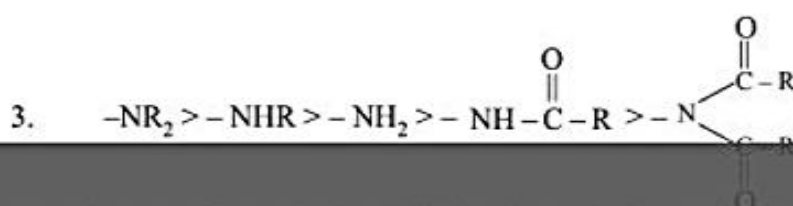
$-\text{CHO}$ ,  $\text{C}=\text{O}$ ,  $-\text{COOH}$ ,  $-\text{NO}_2$ ,  $-\text{CN}$ ,  $-\text{SO}_3\text{H}$ ,  $-\text{SO}_2\text{Cl}$

**Condition :** (i) Vacant orbital must be present

(ii) Multiple bond with more electron negative second atom.

**+ M - effect - order**

- $-\text{CH}_3 > -\text{NH} > -\text{O}^-$
- $-\text{NH} > -\text{NH}$



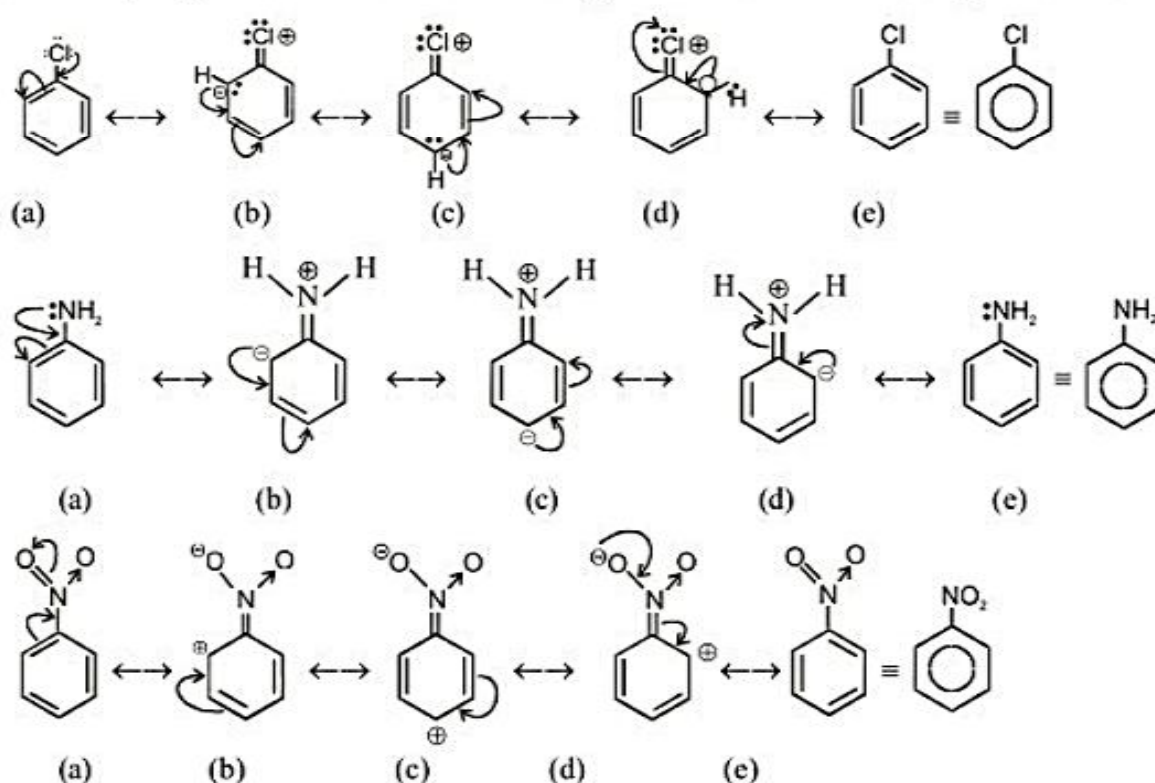


4.  $-\text{O}^- > -\text{OR} > -\ddot{\text{O}}-\text{CH}=\text{CH}_2$
5.  $-\text{NH}_2 > -\text{OH} > -\text{F}$
6.  $-\text{F} > -\text{Cl} > -\text{Br} > -\text{I}$

**- M - effect order**

1.  $-\ddot{\text{C}}\text{H}_2 > -\text{BH}_2 > -\ddot{\text{P}}\text{H}_2$
2.  $-\text{N} \begin{smallmatrix} \text{O} \\ \parallel \\ \text{O} \end{smallmatrix} > -\text{CN} > -\text{C} \begin{smallmatrix} \text{O} \\ \parallel \\ \text{O} \end{smallmatrix} \text{H} > -\text{C} \begin{smallmatrix} \text{O} \\ \parallel \\ \text{O} \end{smallmatrix} \text{R} > -\text{C} \begin{smallmatrix} \text{O} \\ \parallel \\ \text{O} \end{smallmatrix} \text{OR} > -\text{C} \begin{smallmatrix} \text{O} \\ \parallel \\ \text{O} \end{smallmatrix} \text{NH}_2$

The various resonating structures of chlorobenzene, aniline and nitrobenzene are illustrated in following diagrams. Note that  $-\text{Cl}$  and  $-\text{NH}_2$  show + M effect and  $-\text{NO}_2$  show - M effect.



**Note :**

- (i) Thus, mesomeric effect works at only ortho & para position, it is absent on meta position, while inductive effect works at all three position o, m, p however intensity of effect decreases as the distance increases.
- (ii) Mesomeric effect always dominates on inductive effect except halogen (Cl, Br, I, only).

**APPLICATION OF MESOMERIC EFFECT**

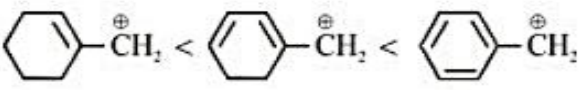
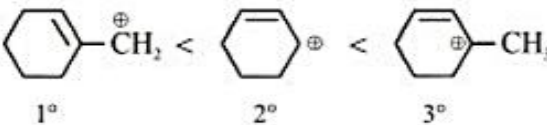
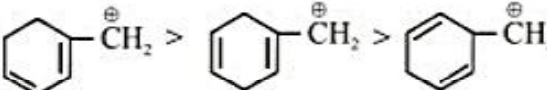
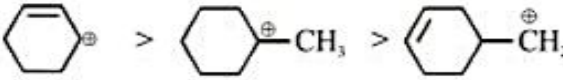
**Stability of reaction intermediates**

**(i) Stability of carbocation**

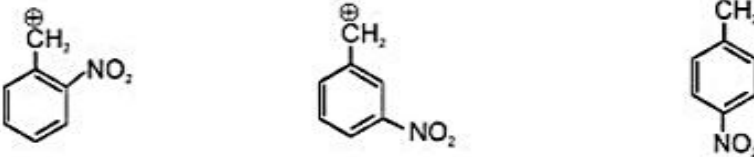
- More resonance in carbocation, more stability of carbocation.
- Aromatic cations are more stable than non aromatic cations.

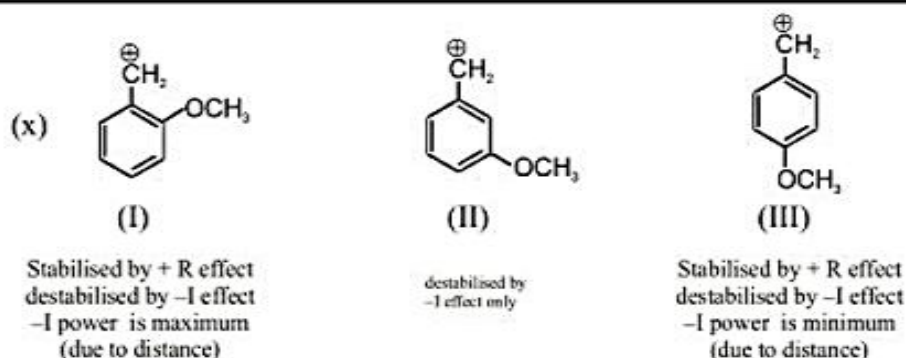


**Example:** Stability order :

- (i)  $\text{CH}_3 - \overset{\oplus}{\underset{\text{CH}_3}{\text{C}}} - \text{CH} = \text{CH}_2 > \text{CH}_3 - \overset{\oplus}{\text{C}}\text{H} - \text{CH} = \text{CH}_2 > \overset{\oplus}{\text{C}}\text{H}_2 - \text{CH} = \text{CH}_2$
- (ii)  $\text{CH}_2 = \text{CH} - \overset{\oplus}{\text{C}}\text{H}_2 > \text{CH}_3 \rightarrow \text{CH}_2 - \overset{\oplus}{\text{C}}\text{H}_2 > \text{CH}_2 = \text{CH} - \text{CH}_2 \leftarrow \overset{\oplus}{\text{C}}\text{H}_2$
- (iii) 
- (iv)   
1°                      2°                      3°
- (v) 
- (vi)  $(\text{C}_6\text{H}_5)_3\overset{\oplus}{\text{C}} > (\text{C}_6\text{H}_5)_2\overset{\oplus}{\text{C}}\text{H} > \text{C}_6\text{H}_5\overset{\oplus}{\text{C}}\text{H}_2 > \text{CH}_2 = \text{CH} - \overset{\oplus}{\text{C}}\text{H}_2 > (\text{CH}_3)_3\overset{\oplus}{\text{C}} > (\text{CH}_3)_2\overset{\oplus}{\text{C}}\text{H} > \text{CH}_3 - \overset{\oplus}{\text{C}}\text{H}_2 > \overset{\oplus}{\text{C}}\text{H}_3 > \text{CH}_2 = \overset{\oplus}{\text{C}}\text{H} > \text{CH} \equiv \overset{\oplus}{\text{C}}$
- (vii) 
- (viii)  $\text{CH}_2 = \text{CH} - \overset{\oplus}{\text{C}}\text{H}_2$                        $\text{C}_6\text{H}_5 - \overset{\oplus}{\text{C}}\text{H}_2$   
allyl carbocation                      benzyl carbocation  
Number of resonating                      Number of resonating  
Structures = 2                      Structures = 4

Hence the benzyl carbocation is more stable than the allyl carbocation.

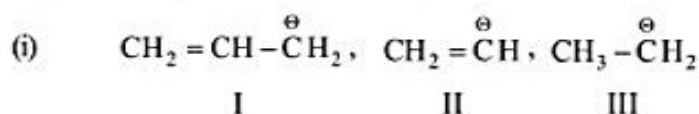
- (ix)   
(I)                      (II)                      (III)  
Increase in                      Increase in                      Increase in  
positive charge by                      positive charge                      Positive charge by  
-I and -R effect                      only by -I effect                      -I and -R effect  
stability order II > III > I



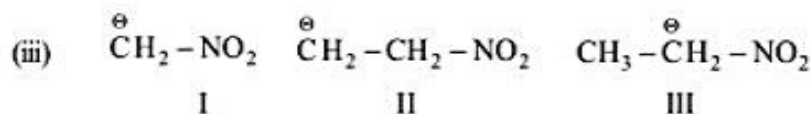
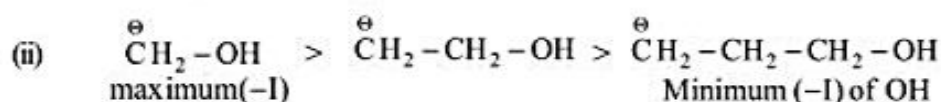
stability order III > I > II

**(ii) Stability of carbanion : More resonance in carbanion, more stability of carbanion**

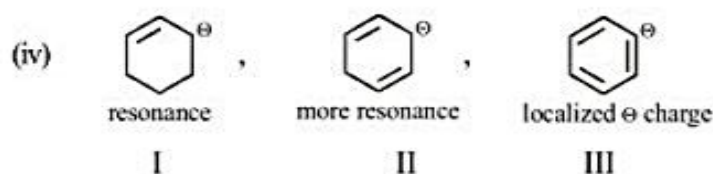
**Example:** stability order for following



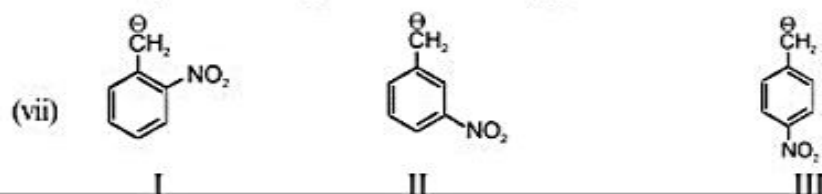
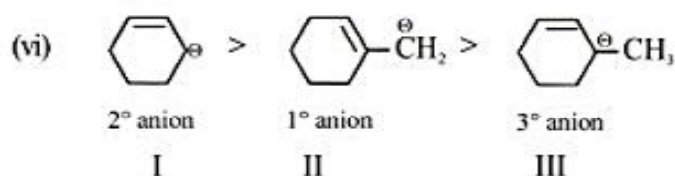
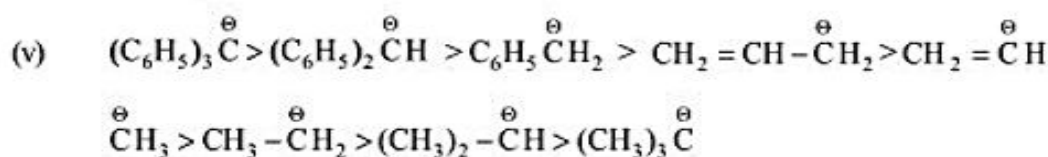
stability order I > II > III



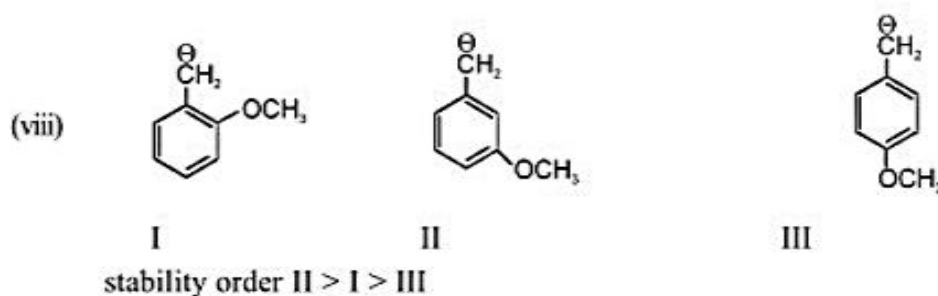
stability order I > III > II



stability order II > I > III



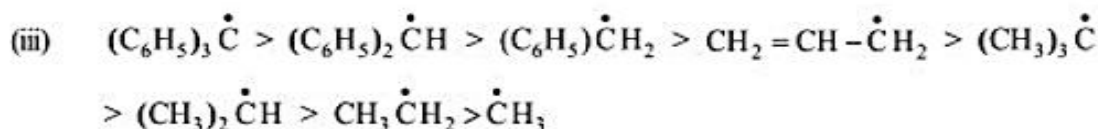
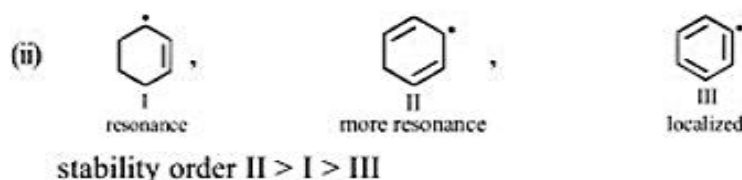
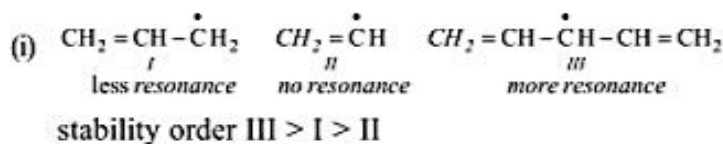
stability order I > III > II



(iii) **Stability of free radicals.**

- More resonance, more stability of free radical.

**Example: Stability order**



## ACIDIC STRENGTH

For an acid  $\text{HA}_{(\text{aq})} \rightleftharpoons \text{H}^+_{(\text{aq})} + \text{A}^-_{(\text{aq})}$

from law of mass action,  $K_a = \frac{[\text{H}^+_{(\text{aq})}][\text{A}^-_{(\text{aq})}]}{[\text{HA}]}$

where,  $K_a \rightarrow$  Acidity constant, or dissociation constant of acid

$K_a \rightarrow$  Explain the strength of acid

$$\text{p}K_a = -\log K_a, \quad K_a \propto \text{Acidic strength} \propto 1/\text{p}K_a$$

$$\text{pH} = -\log [\text{H}^+]$$

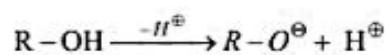
$$\text{Acidic strength} \propto \text{stability of conjugate base} \propto -\text{M effect} \propto \frac{I}{+M} \propto -I \propto \frac{I}{+I}$$

Acidity of Phenol v/s alcohol



Phenol

stabilized by resonance



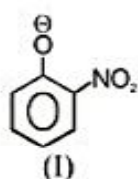
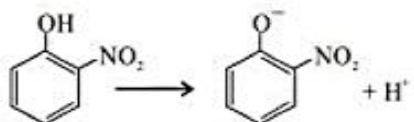
Alcohol

no resonance

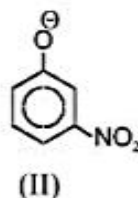
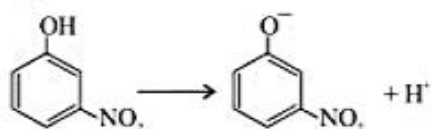
thus acidic strength of phenol &gt; alcohol

more is the stability of phenoxide ion more will be the acidity of phenol

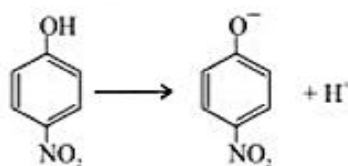
**Acidity of Substituted Phenols :** Acidity of substituted phenols depend on the stability of the phenoxide ion because acidity is the function of conjugate base.



Stabilised by -R and -I  
effect and -I  
power is maximum



Stabilised by -I  
effect only

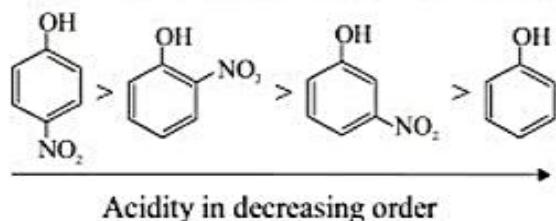


Stabilised by -R and -I  
effect and -I  
power is maximum

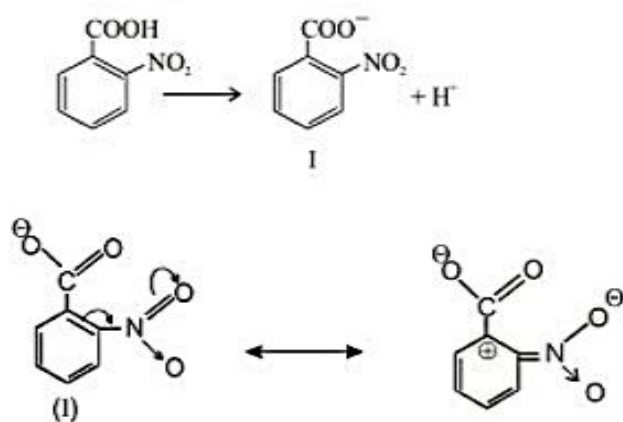
stability order should be I > III > II



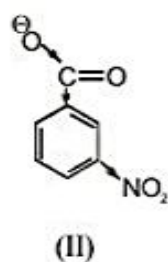
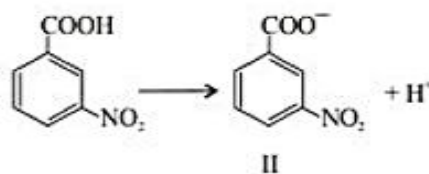
Thus according to stability of anions o-derivative will be more acidic than p-derivative which will be more acidic than m-derivative. But result is as follows in case of nitrophenols, p-derivative is more acidic than o-derivative which is more acidic than m-derivative. In o-derivative, there is intramolecular hydrogen bonding which decrease acidity. Thus order of acidity is as follows :



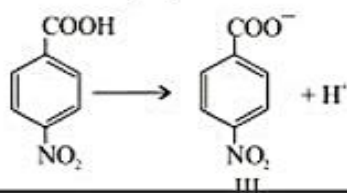
**Acidity of substituted benzoic acids** Ortho substituted benzoic acid is always a stronger acid than m- and p-derivative. This is known as ortho effect

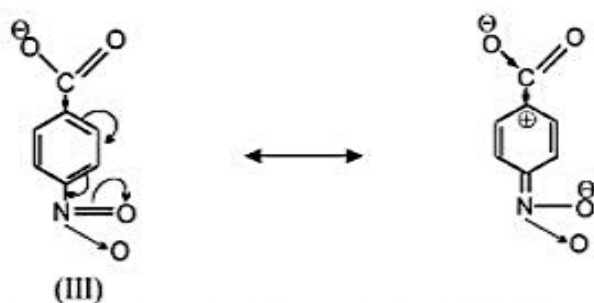


Thus, anion is stabilised by -R and -I effect and -I power is maximum.

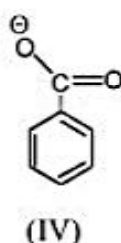
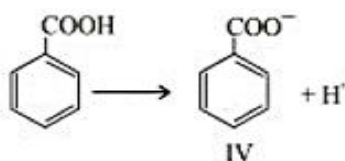


Anion is stabilised only by -I effect of  $\text{NO}_2$  group



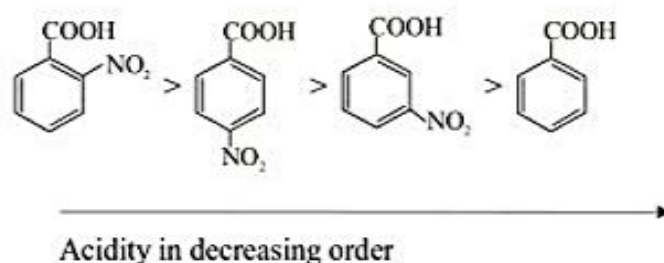


Anion is stabilised by -R and -I effect of  $\text{NO}_2$  group



Thus decreasing order of the stability of these anions is follows :  $\text{I} > \text{III} > \text{II} > \text{IV}$

We know that ortho derivative is the most acidic therefore decreasing order of acidity of these acids is as follows :



## BASIC STRENGTH

For an base,  $\text{BOH}_{(\text{aq})} \rightleftharpoons \text{B}^+_{(\text{aq})} + \text{OH}^-_{(\text{aq})}$

from law of mass action,  $K_b = \frac{[\text{B}^+_{(\text{aq})}][\text{OH}^-_{(\text{aq})}]}{[\text{BOH}]}$

where,  $K_b \rightarrow$  Basicity constant, or dissociation constant of base

$K_b \rightarrow$  Explains the strength of base

$K_b \propto \text{Basic strength} \propto 1/pK_b$

$pK_b = -\log K_b$

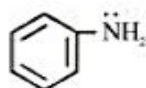
$pOH = -\log [\text{OH}^-]$

$$\text{basic strength} \propto +M \propto \frac{1}{-M} \propto +I \propto \frac{1}{-I}$$

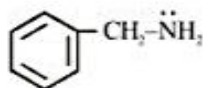
**Basicity of Aromatic Amines :** Basicity of nitrogen containing compounds  $\propto$  Electron density on nitrogen.

In aromatic amines, lone pair of electrons present on nitrogen is delocalised, hence electron density decrease due to resonance.

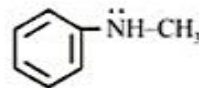
Ex.  $\text{C}_6\text{H}_5\text{NH}_2$  is less basic than  $\text{CH}_3\text{NH}_2$



lone pair is participating in resonance  
(I)



no resonance of lone pair  
so maximum basic  
(II)



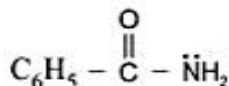
lone pair is participating in resonance  
and +I of  $\text{CH}_3$   
(III)

basic order  $\text{II} > \text{III} > \text{I}$

**Effect of cross conjugation on basicity :**



Due to delocalisation and  $-I$  effect of  $\text{C}=\text{O}$  group, amides are less basic than amines.



In this amide there is cross conjugation which increases basicity; thus  $\text{C}_6\text{H}_5\text{CONH}_2$  is more basic than  $\text{CH}_3\text{CONH}_2$ .  $\pi$  bond of  $\text{C}=\text{O}$  group is in conjugation to benzene ring as well as lone pair of  $\text{NH}_2$  group.

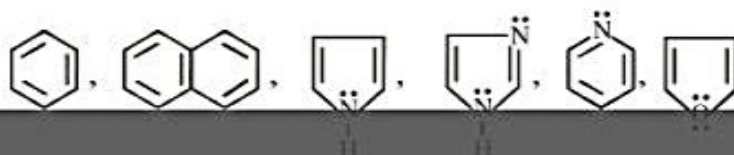
## AROMATICITY

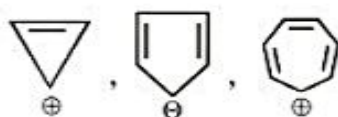
(a) **Aromatic Character of Compounds :** According to the **Huckel rule**, a compound will be aromatic if it fulfils the following four conditions :

- Compound should be cyclic
- Compound should be planar or nearly planar.
- Compound should be conjugated through out ring
- Compound should have  $(4n + 2)\pi$  conjugated or delocalised electrons where  $n$  is a whole number

	$n = 0,$	$1,$	$2,$	$3,$	$4,$	$5, \dots$
$(4n + 2)\pi$ electron	$= 2$	$6$	$10$	$14$	$18$	$22, \dots$

Examples :



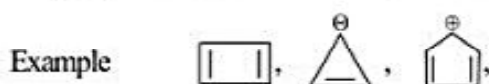


(b) **Antiaromatic Compounds** : According to Huckel rule, compound will be antiaromatic if it fulfils the following four conditions :

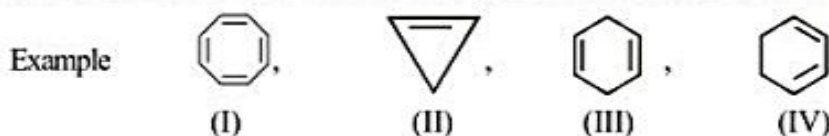
- Compound should be cyclic
- Compound should be planar.
- Compound should be conjugated through out ring and
- Compound should have  $(4n)\pi$  conjugated or delocalised electrons where  $n$  is a whole number

$$n = 1, 2, 3, 4, 5, 6$$

	$n =$	1,	2,	3,	4,	5.....
$(4n)\pi$ electron	$=$	4	8	12	16	20.....



(c) **Non aromatic compounds** : these compounds are neither aromatic nor antiaromatic



Although cyclooctatetraene has  $(4n)\pi$  electrons but even then it is not an antiaromatic. Geometry of this compound is non planar. Thus it is non aromatic. II<sup>nd</sup>, III<sup>rd</sup> & IV<sup>th</sup> compounds are not completely conjugated.

**Note** : Due to Aromaticity extra stability is achieved by aromatic molecule, than non-aromatic or antiaromatic molecule.

(E) **Bond order** : Bond order in conjugated compound or bond order in compounds which exhibit resonance

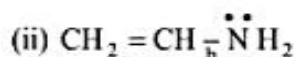
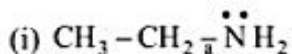
$$\text{Bond order} = \frac{\text{Total number of bonds between two atoms}}{\text{Number of resonating structures}}$$

For examples :



$$\text{Bond order of carbon in benzene} = \frac{2+1}{2} = 1.5$$

**Example** : Give the correct order of bond length of following mentioned compounds.



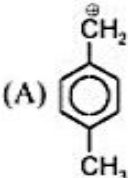
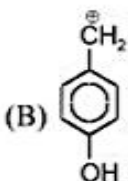
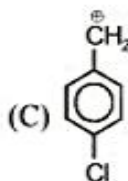
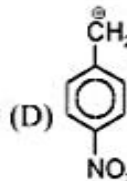
no resonance (only single bond characters)      resonance (partial double bond characters)  
bond length order :  $a > b$



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**MCQ**


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- Q.1** Which of the following carboxylic acids is most acidic in character -  
 (A) o-methyl benzoic acid (B) m-methyl benzoic acid  
 (C) p-methyl benzoic acid (D) Benzoic acid
- Q.2** Which one of the following is most acidic-  
 (A) p-nitrophenol (B) phenol (C) m-nitrophenol (D) o-nitrophenol
- Q.3** Consider the follownig carbocations -  
 (a)  $\text{CH}_3-\text{CH}_2^+$  (b)  $\text{CH}_2=\text{CH}^+$  (c)  $\text{CH}_2=\text{CH}-\text{CH}_2^+$  (d)  $\text{C}_6\text{H}_5-\text{CH}_2^+$   
 Stability of these carbocations in decreasing order is -  
 (A)  $d > c > a > b$  (B)  $d > c > b > a$  (C)  $c > d > b > a$  (D)  $c > d > a > b$
- Q.4** Increasing order of acid strength among p - methoxy phenol, p-methyl phenol and p-nitrophenol is-  
 (A) p- nitrophenol, p-methoxyphenol, p- methylphenol  
 (B) p- methylphenol, p- methoxyphenol, p-nitrophenol  
 (C) p- nitrophenol, p- methylphenol, p- methoxyphenol  
 (D) p- methoxyphenol, p- methylphenol, p- nitrophenol.
- Q.5** The groups which when present in para position tend to decrease the acidity of phenol are-  
 (A)  $-\text{NO}_2$  (B)  $-\text{CN}$  (C)  $-\text{OCH}_3$  (D)  $-\text{F}$
- Q.6** Which free radical is the most stable -  
 (A)  $\text{C}_6\text{H}_5-\dot{\text{C}}\text{H}_2$  (B)  $\text{CH}_2=\text{CH}-\dot{\text{C}}\text{H}_2$  (C)  $\text{CH}_3-\dot{\text{C}}\text{H}-\text{CH}_3$  (D)  $\text{CH}_3-\dot{\text{C}}(\text{CH}_3)-\text{CH}_3$
- Q.7** Which carbocation is the most stable -  
 (A)  (B)  (C)  (D) 

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**ANSWERS**

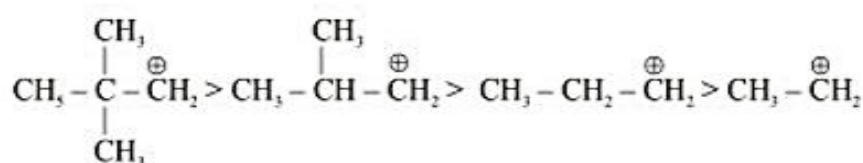

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Q.1 A    Q.2 A    Q.3 A    Q.4 D    Q.5 C    Q.6 A    Q.7 B.

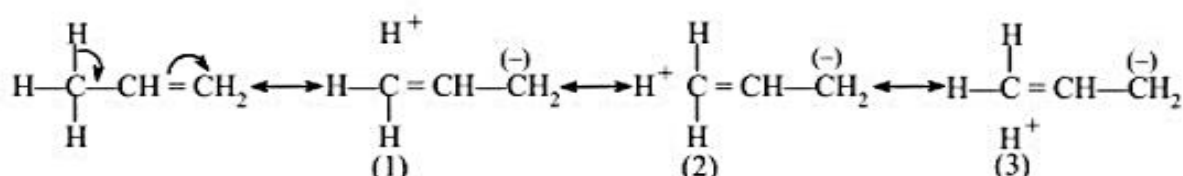
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**HYPER CONJUGATION**
**Introduction**

According to inductive effect order of stability of cations should be



But actually order should be reversed which is explained on the basis of hyper conjugation.



**Definition :-** Delocalization of conjugated (C-H) sigma electrons with  $\pi$ -bond or positive charge or free radical is called hyperconjugation or H-effect.

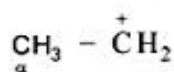
- (i) hyperconjugating structures may be written involving "no bond" between the alpha carbon and hydrogen atoms so known as "no bond resonance."
- (ii) Nathan baker observed this effect so known as "Nathan baker effect"
- (iii) It is also permanent effect

#### Condition for hyperconjugation:

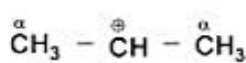
- (i) Compound should have at least one  $\text{sp}^2$ -hybrid carbon of either alkene, alkyl carbocation or alkyl free radical.
- (ii)  $\alpha$ -carbon with respect to  $\text{sp}^2$  hybrid carbon should have at least one hydrogen. If both these conditions are fulfilled then hyperconjugation will take place in the molecule.

#### TYPES OF HYPERCONJUGATION

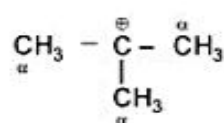
- (i)  **$\sigma$  (C - H), vacant orbital (positive charge) hyperconjugation :** This type of conjugation occurs in alkyl carbocation.



no. of  $\alpha$  H = 3

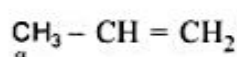


no. of  $\alpha$  H = 6

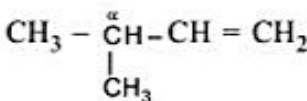


no. of  $\alpha$  H = 9

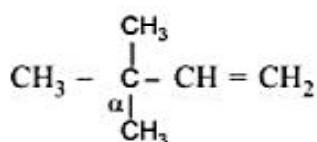
- (ii)  **$\sigma$  (C - H),  $\pi$  hyperconjugation :** This type of conjugation occurs in alkenes.



no. of  $\alpha$  H = 3

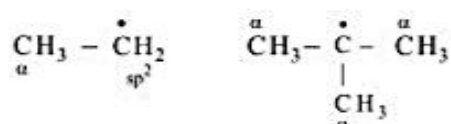


no. of  $\alpha$  H = 1



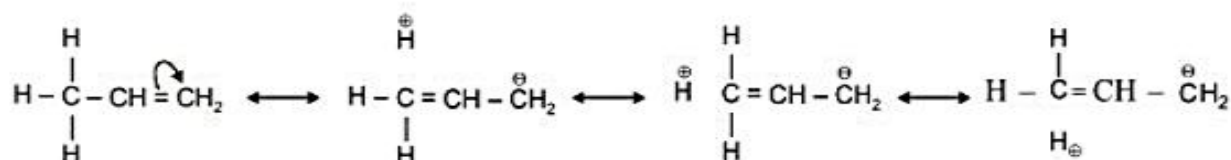
no. of  $\alpha$  H = 0

- (iii)  **$\sigma$  (C - H), odd electron hyperconjugation :** This type of conjugation occurs in alkyl free radicals -



**Note:** Carbanion never shows hyper conjugation, if there is one  $\text{-C-H}$  sigma bond alternate with negative charge then there will be no H-effect

Hyper conjugating structures due to hyperconjugation may be written involving "no bond" between the alpha carbon and hydrogen atoms.

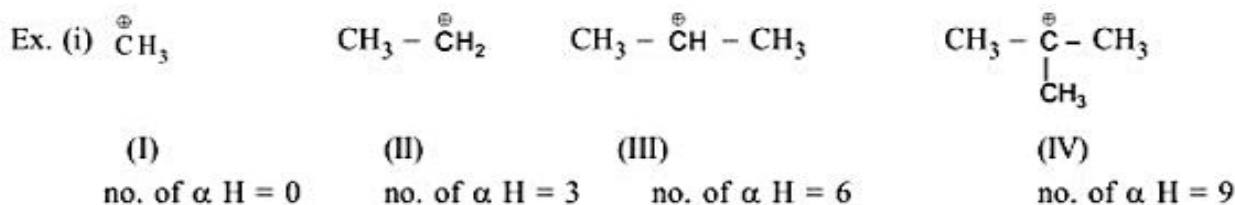


In the above hyper conjugating structures there is no covalent bond between carbon and hydrogen. From this point of view, hyperconjugation may be regarded as "no bond resonance".

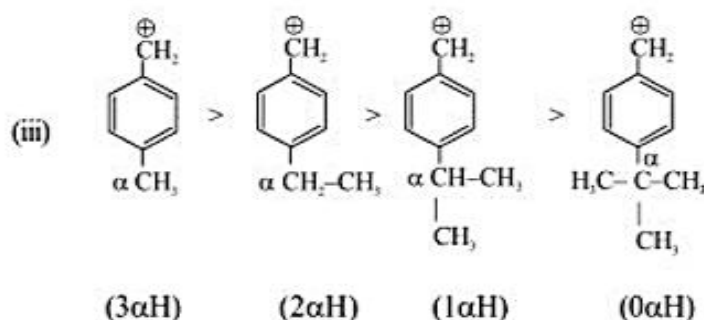
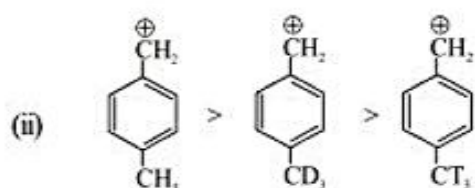
order of effectiveness of hyperconjugation :  $\alpha \text{ C-H bond} > \alpha \text{ C-D bond} > \alpha \text{ C-T bond}$

## APPLICATION OF HYPERCONJUGATION

(A) **Stability of Alkyl Carbocations :** Stability of alkyl carbocations  $\propto$  number of hyperconjugating structures  $\propto$  number of  $\alpha$ -hydrogens.



stability order  $\text{IV} > \text{III} > \text{II} > \text{I}$

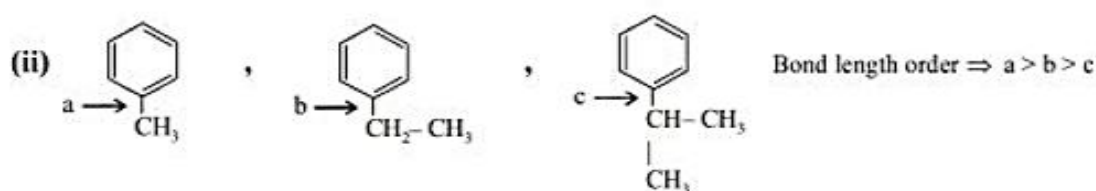


(H effect dominates over I effect)

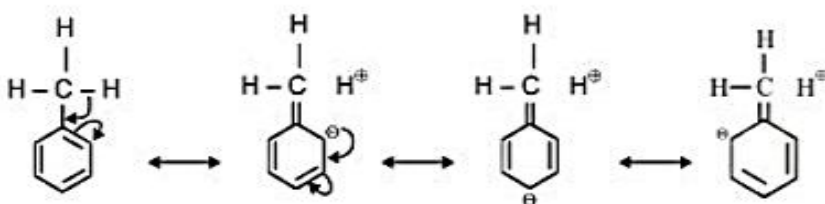




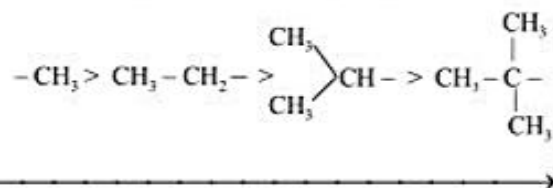




- (E) **Electron releasing (or donating) power of (-R) in alkyl benzene :**  $\text{CH}_3$  - (or alkyl group) is +H group, ortho-para directing group and activating group for electrophilic aromatic substitution reaction because of the hyperconjugation.



The electron donating power of alkyl group will depend on the number of hydrogens present on  $\alpha$ -carbon. The electron releasing power of some groups are as follows -



Electron donating power in decreasing order due to the hyperconjugation

- (F) **Heat of hydrogenation (HOH) :**

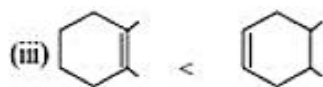
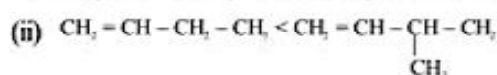
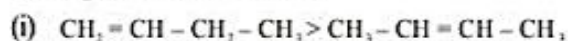


- (a) heat evolved when 1 mole of any unsaturated hydrocarbon are hydrogenated is called heat of hydrogenation ( $\Delta\text{H}$ ) If alkene is more reactive towards hydrogen then it will evolve more  $\Delta\text{H}$ .

$$\text{So, } \Delta\text{H} \propto \frac{1}{\text{stability of alkene}} \propto \frac{1}{\text{number of } \alpha\text{-H}}$$

- (b)  $\Delta\text{H} \propto \text{number of } \pi \text{ bonds}$   
 (c) It is exothermic process (energy release)

Examples of HOH order

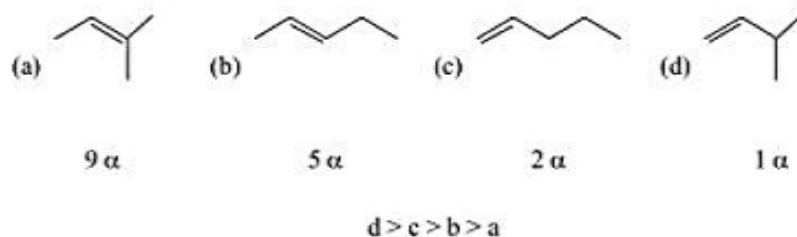


### Heat of combustion (HOC)

It is the energy liberated during complete combustion of organic compound.

**HOC comparison**

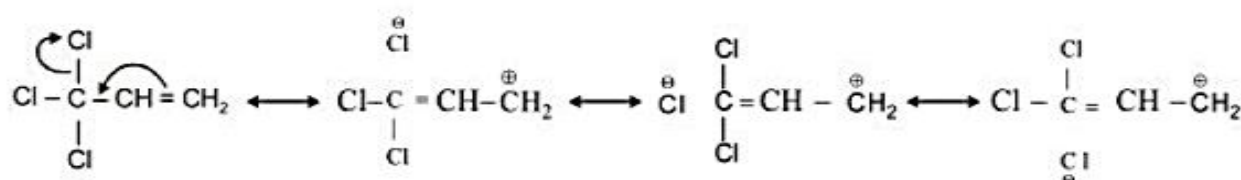
$$\text{HOC} \propto \text{No. of carbon-atoms}$$


$$\text{HOC} \propto \frac{1}{\text{Stability of hydrocarbon}}$$
**Note : Reverse Hyperconjugation (-H effect) :**

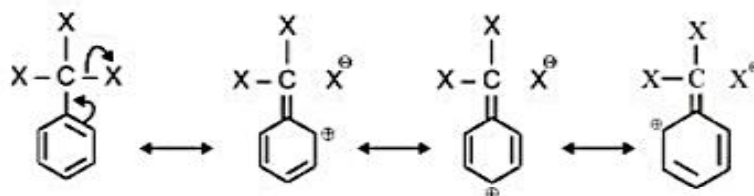
The phenomenon of hyperconjugation is also observed in the system given below :



In such system the effect operates in the reverse direction. Hence the hyperconjugation in such system is known as reverse hyperconjugation.

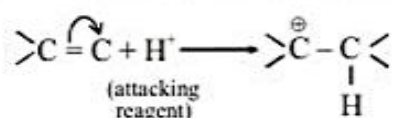


The meta directing influence and deactivating effect of  $-\text{CX}_3$  group for electrophilic aromatic substitution reaction can be explained by this effect.

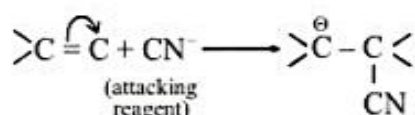
**ELECTROMERIC EFFECT : (E-EFFECT)**

- It is temporary effect.
- The organic compounds having a unsaturation (a double or triple bond) show this effect in the presence of an attacking reagent only. It is defined as the complete transfer of a shared pair of electrons to one of the atoms joined by a multiple bond on the demand of an attacking reagent.

- The effect is annulled as soon as the attacking reagent is removed from the domain of the reaction.
  - It is represented by E and the shifting of the electrons is shown by a curved arrow ( $\curvearrowright$ ).
  - When inductive and electromeric effect operate in opposite directions, the electromeric effect predominates.
  - There are two distinct types of electromeric effect.
- (i) **Positive Electromeric Effect (+E effect)** : In this effect the  $\pi$ -electrons of the multiple bond are transferred to that atom to which the reagent gets attached. For example :



- (ii) **Negative Electromeric Effect (-E effect)** : In this effect the  $\pi$ -electrons of the multiple bond are transferred to that atom to which the attacking reagent does not get attached. For example.



## ATTACKING REAGENTS

The species which attack on a substrate and form a product is called as attacking reagents.

**Substrate** - Reactant which is less reactive is generally taken in greater amount.

Attacking reagents are of two types

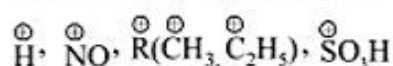
- (A) Electrophile (B) Nucleophile

### (A) Electrophiles or electrophilic reagents ( $E^{\oplus}$ ):

- They are electron deficient species.
- They have a tendency to accept electron from another molecule
- In a reaction, an electrophile attacks the substrate at the point of maximum electron density.
- Neutral molecule having electron deficient centre,  $\text{CCl}_4$ ,  $\text{CO}_2$

### Types of Electrophile :

- (i) Positively charged electrophiles



- (ii) Neutral electrophiles

- All Lewis acids as :  $\text{BF}_3$ ,  $\text{AlCl}_3$ ,  $\text{SO}_3$ ,  $\text{ZnCl}_2$ ,  $\text{BeCl}_2$ ,  $\text{FeCl}_3$ ,  $\text{SnCl}_4$
- Free radicals, carbenes acts as electrophiles.
- Transition metal cations are electrophiles, e.g.  $\text{Fe}^{3+}$ ,  $\text{Fe}^+$ ,  $\text{Ag}^+$ ,  $\text{Cd}^{2+}$  etc.]
- Neutral molecule having electron deficient center, eg.  $\text{CCl}_4$ ,  $\text{CO}_2$



**(B) Nucleophilic reagents or nucleophiles :**

- (a) They are electron rich species so they have a tendency to donate electron pair.
- (b) All nucleophiles are lewis bases.
- (c) They attack the centre of minimum electron density in a molecule in a chemical reaction.

**Types of Nucleophile :****(i) Negatively Charged nucleophiles :**

$F^-$ ,  $Cl^-$ ,  $Br^-$ ,  $I^-$ ,  $OH^-$ ,  $CN^-$ ,  $RCOO^-$ ,  $RO^-$ ,  $R^-$ ,  $R-C \equiv C^-$ ,  $NH_2^-$ ,  $SH^-$  etc.

**(ii) Neutral nucleophile containing lone pair :**

$H_2\ddot{O}$ ,  $R-\ddot{O}H$ ,  $R-\ddot{O}-R$ ,  $\ddot{N}H_3$ ,  $R-\ddot{N}H_2$

**(iii)  $\pi$  electron containing compounds**

$CH_2=CH_2$ ,  $CH \equiv CH$

**(C) Ambiphiles :**

Ambiphiles are those which act as both electrophile and nucleophile.

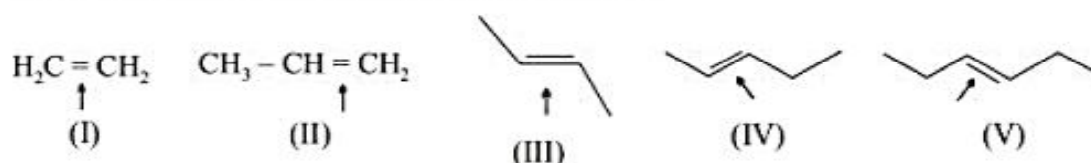
*Example :*

$R-CH=\ddot{O}$ ,  $RCOR$ ,  $RCOOH$  etc.

S. No.	Electrophile	Nucleophile
1	Accept electron	Supplies the electron pair
2	Electron deficient (electron loving)	Electron rich
3	Usually positively charged species	Usually negatively charged species
4	Attacks the points of high electron density	Attacks the point of low electron density
5	e.g., $H^+$ , $CH_3^+$ , $CO_2^+$ , $NO^+$	e.g., $F^-$ , $Cl^-$ , $Br^-$ , $I^-$ , $H_2O$

**MCQ**

**Q.1** Find out the correct statement(s) about given compound



- (A) Order of Heat of Hydrogenation & Heat of combustion is same
- (B) Order of Heat of Hydrogenation & Heat of combustion is different
- (C) Order of rotation barrier energy for marked bond is  $I > II > V > IV > III$
- (D) Order of Boiling point is  $V > IV > III > II > I$



## GASEOUS STATE

### 1. INTRODUCTION

A given substance may occur in solid, liquid or gaseous phase depending upon the relative value of two tendencies namely Mutual Attraction (MA) and Escaping Tendency (ET)

- (i) if MA is greater than ET then substance will occur in solid state
  - (ii) if MA is slightly greater than ET then substance will occur in liquid state
  - (iii) if MA is very much less than ET then substance will occur in gaseous state
- Out of the three states of matter, we will study the gaseous state.

This state of matter is characterized by sensitivity of volume change with change of pressure and temperature. It is due to large distance between molecules as compared to their own dimensions.

Gaseous state can be defined as collection of molecule far apart and continuously in motion.

### 2. MEASURABLE PROPERTIES OF GASES

**2.1 Mass :** The mass of gas is generally used in the form of number of moles which is related as

$$(i) \quad \text{no. of moles} = \frac{\text{wt. in gm}}{\text{molecular mass of gases}} \quad \left( n = \frac{w}{M} \right)$$

Two other useful formulae to calculate number of moles of gas are –

$$(ii) \quad \text{number of moles} = \frac{\text{no. of molecules of given gas}}{\text{Avogadro's number of molecules}} \quad \left( n = \frac{N}{N_A} \right)$$

$$(iii) \quad \text{no. of moles} = \frac{\text{volume of given gas in litres at STP}}{22.4 \text{ L}}$$

**2.2 Volume :** Volume of gas is volume of the container in which it is present, i.e. space which the gas molecules can occupy.

**Relation between different units of volume**

$$1 \text{ m}^3 = 10^3 \text{ dm}^3 = 10^3 \text{ litre} = 10^6 \text{ cm}^3 = 10^6 \text{ ml} = 10^9 \text{ mm}^3.$$

**2.3 Temperature :** Degree of hotness or coldness of a body is measured by temperature

$$\frac{C}{100} = \frac{K - 273}{100} = \frac{F - 32}{180}$$

C – Celcius scale,      K – Kelvin scale,      F – Fahrenheit scale

**Note :** In all the problems of gaseous state (i.e. in all gas law equations), temperature must be expressed in kelvin scale. i.e. ,  $t^{\circ}\text{C} + 273.15 = \text{TK}$

**2.4 Pressure :** Pressure of gas is defined as the force exerted by the gas on the walls of its container. It is often assumed that pressure is isotropic, i.e. it is the same in all the tree directions.

**Units and determination of pressure of gas :**

- (a) In SI unit the unit, of pressure is the pascal ( $\text{N/m}^2$ ) instead, the unit bar, kPa or MPa is used, generally.

$$1 \text{ bar} = 10^5 \text{ N/m}^2 = 100 \text{ kN/m}^2 = 100 \text{ kPa}$$

- (b) Pressure is also stated in mm or cm of mercury.

$$1 \text{ atm} = 760 \text{ mm Hg} = 1.01325 \text{ bar} = 1.01325 \times 10^5 \text{ Pa} = 101.325 \text{ kN/m}^2 = 1.0332 \text{ Kg/cm}^2$$

$$1 \text{ Pa} = 1 \text{ Nm}^{-2} = 1 \text{ Kg m}^{-1} \text{ S}^{-1}$$

$$1 \text{ L} = 1 \text{ dm}^3 = 10^{-3} \text{ m}^3 \text{ (SI unit)}$$

$$1 \text{ L atm} = 101.325 \text{ J}$$

$$1 \frac{\text{KN}}{\text{m}^2} = 1 \times 10^3 \frac{\text{N}}{\text{m}^2} = \frac{1 \times 10^3 \times \text{kg}}{9.8 \times 10^4 \text{ cm}^2} = \frac{1}{98} \text{ kgf/cm}^2$$

$$1 \text{ Torr} = \frac{1}{760} \text{ Pa} = 133.322 \text{ Pa}$$

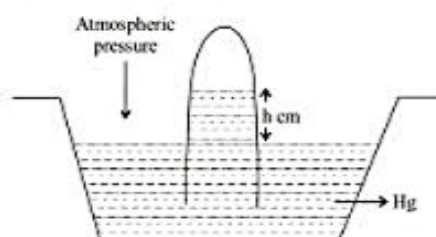
- (c) The pressure relative to the atmosphere is called gauge pressure. The pressure relative to the perfect vacuum is called absolute pressure.

$$\text{Absolute pressure} = \text{Gauge pressure} + \text{Atmosphere pressure}$$

- (d) Pressure is measured using a manometer which is a simple device with a horizontal arm and a U-tube carrying mercury or any other suitable liquid.

**3. MEASUREMENT OF PRESSURE**

- 3.1 Barometer :** The instrument used for the measurement of atmospheric pressure is called Barometer. It consists inverted a tube filled with mercury in a dish of mercury. The height of the mercury column is a measure of the atmospheric pressure at that place.



$$\begin{aligned} \text{vol. of Hg} &= \text{Area} \times \text{Height} \\ &= A \times h \end{aligned}$$

$$\begin{aligned} \text{Mass of Hg} &= \text{Volume} \times \text{Density} \\ &= A \times h \times d \end{aligned}$$

$$\begin{aligned} \text{Force of mercury} &= \text{Mass} \times g \\ &= A \times h \times d \times g \end{aligned}$$

$$\text{Pressure} = \frac{\text{Force}}{\text{Area}} = \frac{A \times h \times d \times g}{A} = h d g$$

$$P = h d g$$

$$h = \frac{P}{d g}$$

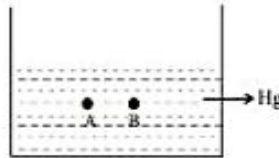
$$P = 1 \text{ atm} = 1.01325 \times 10^5 \text{ Pascal}$$

$$d_{\text{Hg}} = 13.6 \text{ g/ml} = 13.6 \times 10^3 \text{ kg/m}^3$$

$$h = \frac{1.01325 \times 10^5}{13.6 \times 10^3 \times 9.8} = 0.76 \text{ m} = 760 \text{ cm} = 760 \text{ mm}$$

**Note :** 1. Pressure in liquid is independent on cross section area. It only dependent upon height of column.  
2. Pressure at all the points lying on the same horizontal level are always same.

$$P_A = P_B$$



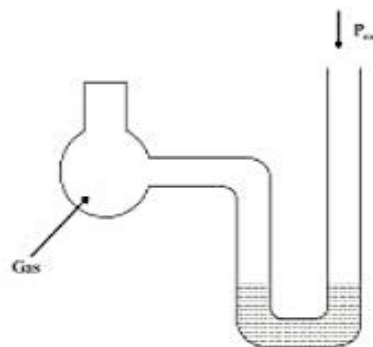
$$P_A - P_B = 0$$

**3.2 Manometer :** The instrument used for the measurement of the pressure of a gas called a manometer. It simply consists of a U shaped tube containing mercury usually. One limb of the tube is longer than the other . Two types of manometers are used. These are

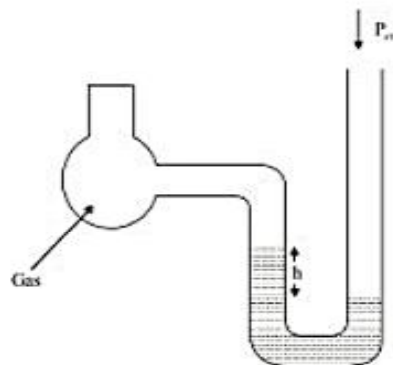
- (i) Open manometer - In this manometer the longer limb is open
- (ii) Closed manometer - In this manometer longer limb is closed

**(I) Open manometer**

(a) if level of Hg in the two limbs is same then  $P_{\text{gas}} = P_{\text{atm}}$



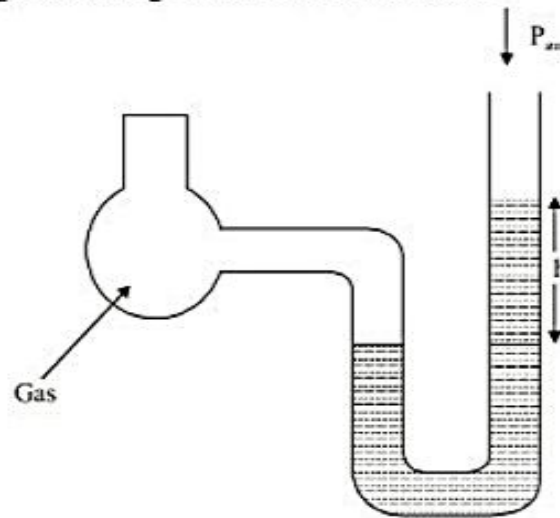
(b) If level of Hg in shorter limb is higher than that of longer limb



$$P_{\text{atm}} = P_{\text{gas}} + h d g$$

$$P_{\text{gas}} = P_{\text{atm}} - h d g$$

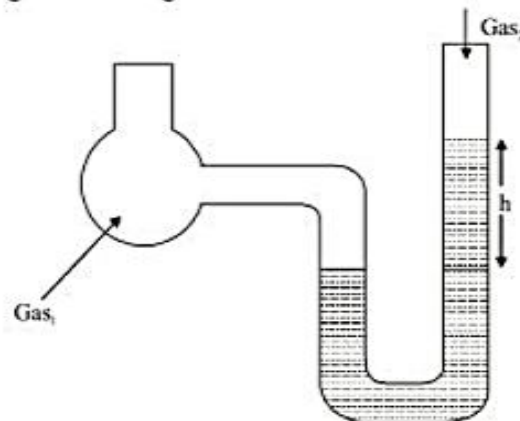
(c) If level of Hg in longer limb is higher than that of shorter limb



$$P_{\text{gas}} = P_{\text{atm}} + h d g$$

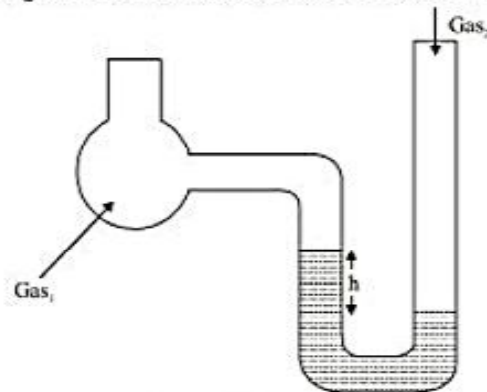
(ii) **Closed Manometer -**

(a) If level of mercury longer limb is higher than that of shorter limb



$$P_{\text{gas}_1} = P_{\text{gas}_2} + h d g$$

(b) If level of mercury in longer limb is lower than that of shorter limb.

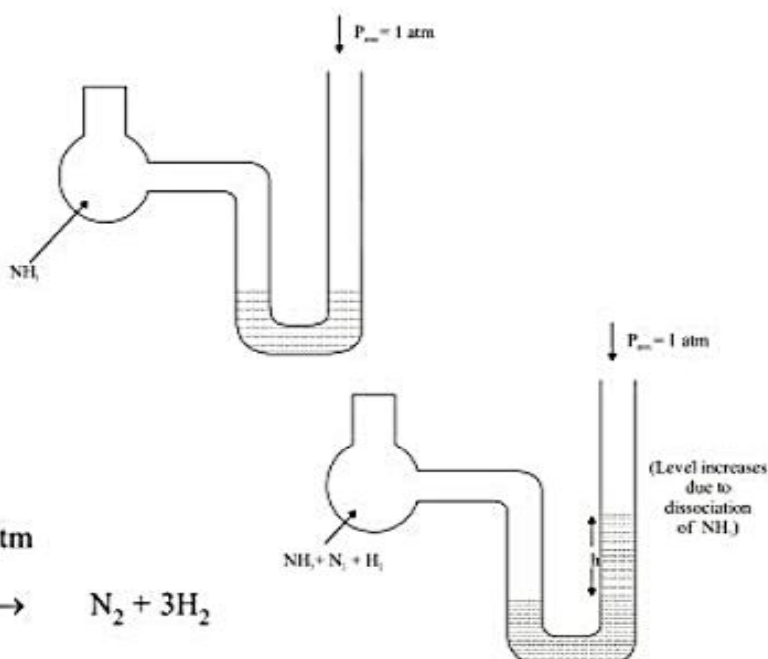


$$P_{\text{gas}_1} + h d g = P_{\text{gas}_2}$$



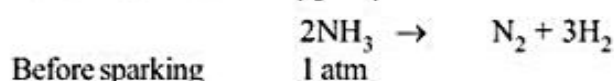
### Illustration

1. A manometer attached to a flask contains  $\text{NH}_3$  gas have no difference in Hg level initially as shown in diagram. After sparking into the flask there is difference of 19 cm in the mercury level in two column manometer. Calculate % dissociation of  $\text{NH}_3$ .



**Sol.**  $P_{\text{NH}_3} = 1 \text{ atm}$

$$P_{\text{NH}_3} + P_{\text{N}_2} + P_{\text{H}_2} = 1 + \frac{19}{76} = \frac{5}{4} \text{ atm}$$



$$\text{After sparking} \quad (1 - P) \quad \frac{P}{2} \quad \frac{3P}{2}$$

$$P_{\text{final}} = 1 - P + \frac{P}{2} + \frac{3P}{2} = \frac{5}{4}$$

$$\text{or } P = \frac{1}{4}$$

$$\% \text{ dissociation} = \frac{1/4}{1} \times 100 = 25\%$$

### Density :

Density may be defined as Mass per unit volume

$$d = \frac{m}{v}$$

### Units :

CGS :  $\text{g/cm}^3$

MKS :  $\text{kg/m}^3$

Relation :  $1 \text{ kg/m}^3 = 10^{-3} \text{ g/cm}^3$

**Note :** 1. Mass, volume and no. of moles are extensive properties (that depend on mass) hence additive in nature.

2. Density, Pressure and Temperature are intensive properties (they does not depend on mass) hence non-additive in nature.

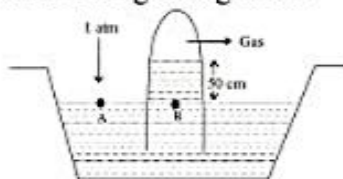
**Illustration**

1. In a barometric tube Hg is replaced by  $H_2O$  then find the height of  $H_2O$  column. Assume that vapour pressure of  $H_2O$  is negligible.

**Sol.**  $h_1 d_1 g = h_2 d_2 g$   $[d_{Hg} = 13.6 \text{ g ml}^{-1}]$   
 $h_1 d_1 = h_2 d_2$   $d_{H_2O} = 1 \text{ g ml}^{-1}]$   
 $76 \times 13.6 = h_2 \times 1$   
 $h_2 = 1033.6 \text{ cm} = 10.336 \text{ m}$

**Note :** Density of Hg is high so column of small height is required.

2. Calculate the pressure of the gas in following arrangement



$P_A = P_B$   
At the equilibrium position

$P_{atm} = P_{gas} + P_{Hg}$   
 $76 \text{ cm} = P_{gas} + 50$   $P_{gas} = 26 \text{ cm}$

**Exercise**

An open tank is filled with Hg up to a height of 76 cm.

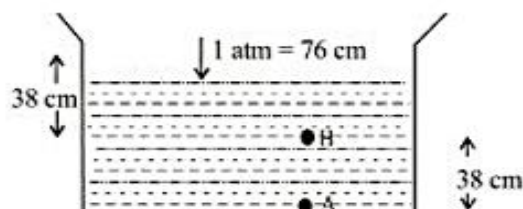
Find the pressure at the

(1) Bottom of the tank

(2) Mid of the tank

Atmospheric pressure = 1 atm

**Ans.** 2 atm, 1.5 atm

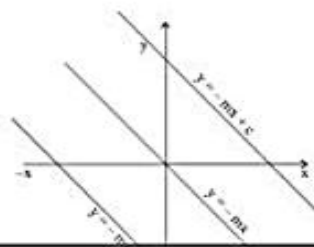
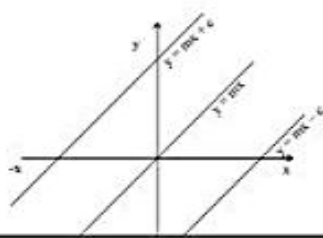
**4. GRAPHICAL ANALYSIS**

Four common equations and their graphical analysis

**(1) Straight line equation**

$y = mx + c$ ,  $m = \text{slope} = \tan \theta$ ,  $c = \text{intercept}$

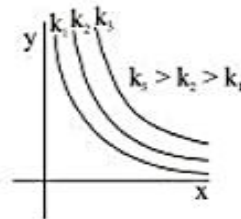
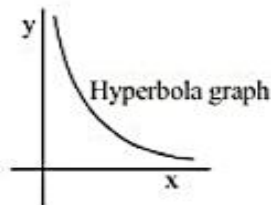
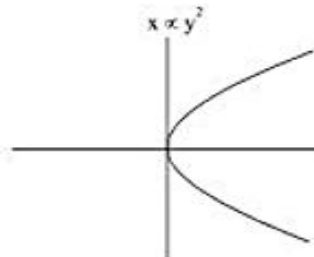
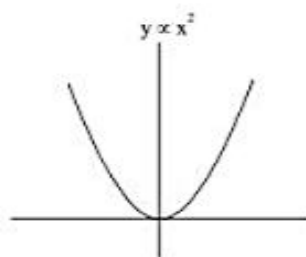
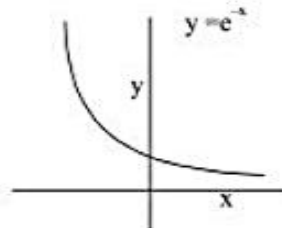
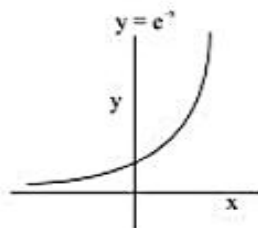
If  $c$  is zero  $\Rightarrow$  straight line passing through origin.



**(2) Hyperbola**

$$yx = \text{constant (k)}$$

$$y = \frac{k}{x} \quad \Rightarrow y \propto \frac{1}{x}$$

**(3) Parabola****(4) Exponential graph****5. GAS LAWS****5.1 Boyle's Law**

It relates the volume and the pressure of a given mass of a gas at constant temperature.

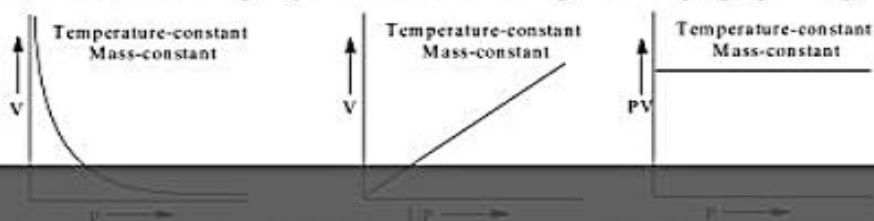
Boyle's law states that, "at constant temperature, the volume of a sample of a gas varies inversely with the pressure".

$$\therefore P \propto \frac{1}{V} \text{ (when temperature and number of moles are kept constant)}$$

The proportionality can be changed into an equality by introducing a constant k, i.e.,

$$P = \frac{k}{V} \text{ or } PV = k$$

Boyle's law can be verified by any one of the following three ways graphically.



Alternatively, Boyle's law can also be stated as follows :

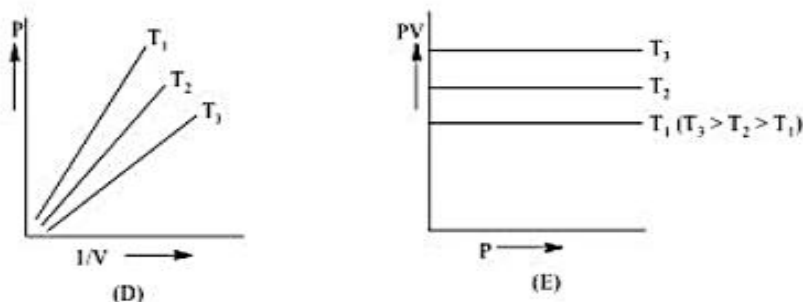
"Temperature remaining constant, the product of pressure and volume of a given mass of a gas is constant".

The value of the constant depends upon the amount of a gas and the temperature.

Mathematically, it can be written as,

$$P_1 V_1 = P_2 V_2 = P_3 V_3 = \dots\dots\dots$$

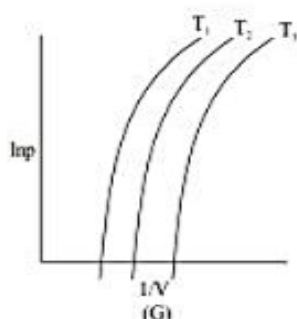
Location of straight line and curve changes with temperature in the **isotherm** shown in the following figure.



According to Boyle's law,  $PV = \text{Constant}$  at constant temperature

$$\therefore \log P + \log V = \text{constant}$$

$$\log P = -\log V = \text{constant}$$



$$PV = k$$

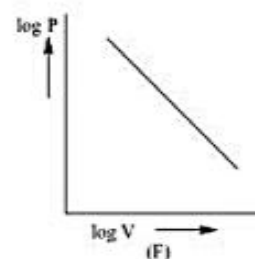
$$\ln P + \ln V = k'$$

$$\ln P = \ln V + k'$$

$$\ln P = -\ln V + k'$$

$$\ln P = \ln 1/V + k'$$

$$y = \ln x + c'$$



### Illustration

1. A gas is present at a pressure of 2 atm. What should be the increase in pressure so that the volume of the gas can be decreased to  $1/4^{\text{th}}$  of the initial value if the temperature is maintained constant.

**Sol.**  $PV = \text{constant}$  for a given mass of gas at constant pressure

$$\Rightarrow P_1 V_1 = P_2 V_2 \quad P_1 = 2 \text{ atm} \quad V_1 = V \quad V_2 = V/4 \quad P_2 = ?$$

$$\text{Now,} \quad 2 \times V = P_2 \times \frac{V}{4} \quad \Rightarrow \quad P_2 = 8 \text{ atm}$$

$\therefore$  Pressure should be increased from 2 to 8 atm

$\therefore$  total increase =  $8 - 2 = 6 \text{ atm}$ .



### Exercise

1. A sample of gas occupies 10 litre under a pressure of 1 atmosphere. What will be its volume if the pressure is increased to 2 atmospheres? Assume that the temperature of the gas sample does not change.

Ans. 5 litre

### 5.2 Charle's law

It states "at constant pressure, the volume of a given mass of a gas, increases or decrease by  $\frac{1}{273.15}$  th of its volume at  $0^\circ\text{C}$  for every rise or fall of one degree in temperature".

$$\frac{V_t}{V_0} = 1 + \frac{t}{273.15} \quad (\text{constant } n \text{ and } P)$$

$$\text{or } V_t = V_0 \left( 1 + \frac{t}{273.15} \right) \quad \text{or } V_t = \frac{V_0(273.15 + t)}{273.15}$$

$0^\circ\text{C}$  on the Celsius scale is equal to 273.15 K at the Kelvin or absolute scale.

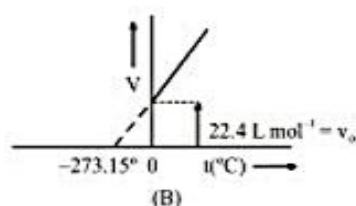
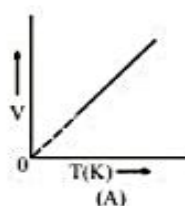
i.e.  $T_1$  (Temperature in Kelvin scale) =  $273.15 + t$

$$\therefore \text{From the above equation we get } \frac{V_t}{V_0} = \frac{T_1}{T_0} \quad \text{or } \frac{V_t}{T_1} = \frac{V_0}{T_0}$$

i.e. The volume of a given gas is proportional to the absolute temperature.

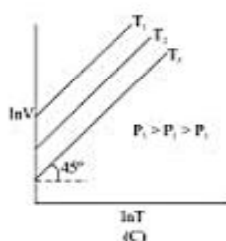
$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \quad (\text{at constant } P)$$

#### Graphical representation :



Graphs between  $V$  and  $T$  at constant pressure are called Isobars.

$\ln V$  vs  $\ln T$



$$\frac{V}{T} = \text{constant (K)}$$

$$V = KT$$

$$\ln V = \ln K + \ln T$$

$$y = C + mx$$

$$m = 1$$

**Illustration**

1. A gas occupies a volume of 580 ml at 17 °C. It is heated to 100 °C at constant pressure. Calculate the volume of the gas -

(A) 746 ml. (B) 760 ml. (C) 773 ml. (D) 780 ml.

Ans. A

Sol. Initial volume ( $V_1$ ) = 580 ml,

$$T_1 = 17 + 273 = 290 \text{ K}$$

Final Volume ( $V_2$ ) = ?

$$T_2 = 100 + 273 = 373 \text{ K}$$

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} ;$$

$$\therefore V_2 = T_2 \times \frac{V_1}{T_1} = 373 \times \frac{580}{290} = 746 \text{ ml.}$$

**Exercise**

1. A gas occupies 3 litres at 32 °C and one atmospheric pressure. What volume will it occupy if the temperature is changed to 18 °C, the pressure remaining constant -

(A) 2.91 litres (B) 2.86 litres (C) 2.30 litres (D) None of these

Ans. B

**5.3 Gay-Lussac's Law**

- (a) It states that at constant volume, the pressure of a given mass of a gas is directly proportional to its absolute temperature.

- (b) Mathematically -  $P \propto T$  (at constant volume)

where  $P$  = pressure of gas

$T$  = Absolute temperature

$$P = KT$$

$$\text{or } \frac{P}{T} = K$$

Hence, if the pressure of a gas is  $P_1$  at temperature  $T_1$  changes to  $P_2$  at  $T_2$ , volume remaining constant.

$$\text{then } \frac{P_1}{T_1} = \frac{P_2}{T_2} = \text{constant}$$

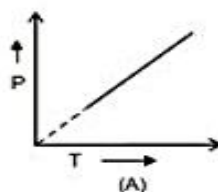
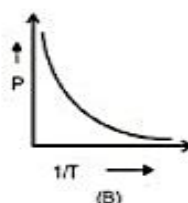
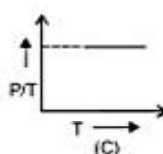
$$\log P - \log T = \text{constant.}$$

$$(c) P_t = P_o \left( 1 + \frac{t}{273.15} \right)$$

where  $P_t$  = Pressure of gas at  $t^\circ\text{C}$

$P_o$  = Pressure of gas at  $0^\circ\text{C}$

## (d) Graphical representation -

(i)  $P$  vs  $T$ (ii)  $P$  vs  $1/T$ (iii)  $P/T$  vs  $V_s T$ 

At constant volume, the pressure of a given amount of a gas is directly proportional to its absolute temperature.

## 5.4 Avagadro's Law

- (a) According to this law under the same condition of temperature and pressure, equal volumes of all gas contains equal no. of molecules.

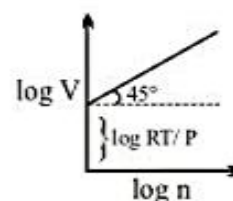
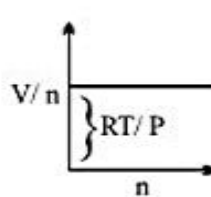
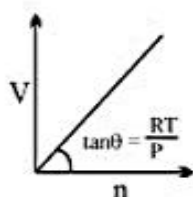
$$V \propto n \text{ (At constant temperature \& pressure)}$$

Where  $V$  = volume

$n$  = no of molecules

- (b) Molar Volume or gram molecular volume is 22.4 litres or 22400 ml of every ideal gas at NTP is the volume occupied by its one gram mole and it is called molar volume or gram molecular volume.
- (c) The mole Concept - Mole is defined as the total amount of substance that contains as many basic units as there are atoms in 12 g of the isotopes of carbon -12. Thus a mole will be defined as the Avogadro no of particles which is equal to  $6.023 \times 10^{23}$ .
- (d) Loschmidt number - It the no of molecules present in the volume of a gas at S.T.P. Its value is  $2.617 \times 10^{19}$  per c.c.

## Avogadro's law

 $V$  vs  $n$  $V/n$  vs  $n$  $\log V$  vs  $\log n$ 

## 6. IDEAL GAS EQUATION

This equation is obtained by combining Boyle's, Charle's and Avogadro's law.

$$V \propto \frac{1}{P} \dots(i) \text{ (at constant temperature and definite mass)}$$

$$V \propto T \dots(ii) \text{ (at constant pressure and definite mass)}$$

$$V \propto n \dots(iii) \text{ (at constant temp and pressure)}$$

Combining eqs. (i), (ii) and (iii)

$$V \propto \frac{1}{P} \times T \times n$$

$$V = R \times \frac{1}{P} \times T \times n$$

$$PV = nRT \dots\dots\dots(1)$$

For 1 mole of the gas  $n = 1$

$$PV = RT$$

$$\text{So } \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} = R \quad \text{or} \quad \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \dots\dots\dots(2)$$

Where  $P_1, V_1, T_1$  are the initial pressure, volume and temperature and  $P_2, V_2, T_2$  are final values. The above equation is called as ideal gas equation.

### 6.1 Ideal gas equation in terms of density

Let  $w$  and  $M$  be the mass and molecular mass of a gas; then

$$n = \frac{w}{M}$$

$$\text{Hence, eq. (1) becomes} \quad PV = \frac{w}{M} RT$$

$$\text{or} \quad P = \frac{w}{M} \cdot \frac{RT}{V} \quad \left[ \frac{w}{V} = \frac{\text{mass}}{\text{Volume}} = \text{Density (d)} \right]$$

$$\text{or} \quad P = \frac{d}{M} RT \dots\dots\dots(3)$$

Eq. (3) is modified form of gas equation. The above equations are strictly followed by ideal gases.

### 6.2 Natures of Molar Gas constant R

Gas equation for one mole of an ideal gas



$$PV = RT$$

or 
$$R = \frac{P \times V}{T} = \frac{\text{Pressure} \times \text{Volume}}{\text{Temperature}}$$

$$\text{Pressure} = \frac{\text{Force}}{\text{Area}} = \frac{\text{Force}}{(\text{Length})^2}$$

$$\text{Volume} = (\text{Length})^3$$

So, 
$$R = \frac{\frac{\text{Force}}{(\text{Length})^2} \times (\text{length})^3}{\text{Temperature}} = \frac{\text{Force} \times \text{Length}}{\text{Temperature}} = \frac{\text{Work}}{\text{Temperature}}$$

Thus, the value of the R should always be expressed in units of work per degree kelvin per mole.

### 6.3 Numerical values of R

$$R = \frac{PV}{T}$$

One gram mole of a gas at one atmospheric pressure and 0°C (273 K) occupies a volume 22.4 litre.

$$P = 1 \text{ atmosphere,}$$

$$T = 273 \text{ K,}$$

$$V = 22.4 \text{ litre}$$

So, 
$$R = \frac{1 \times 22.4}{273} = 0.0821 \text{ litre-atm K}^{-1} \text{ mol}^{-1}$$

If pressure is taken in dyne/cm<sup>2</sup> and volume in mL,  $P = 76 \times 13.67 \times 981 \text{ dyne/cm}^2$ ,  $V = 22400 \text{ mL}$  for 1 mole,  $T = 273 \text{ K}$

So, 
$$R = \frac{76 \times 13.67 \times 981 \times 22400}{273} = 8.314 \times 10^7 \text{ erg K}^{-1} \text{ mol}^{-1}$$

Since, 1 joule = 10<sup>7</sup> erg, so

$$R = 8.314 \text{ joule K}^{-1} \text{ mol}^{-1}$$

Since, 1 calorie = 4.184 × 10<sup>7</sup> erg, so

$$\begin{aligned} R &= \frac{8.314 \times 10^7}{4.184 \times 10^7} \\ &= 1.987 = 2 \text{ calorie K}^{-1} \text{ mol}^{-1} \end{aligned}$$

**Note :** Although, R can be expressed in different unit, but for pressure-volume calculations, R must be taken in the same units of pressure and volume.

**Illustration**

1. Pressure of gas contained in a closed vessel is increased by 0.4%, when heated by 1°C. Calculate its final temperature. Assume ideal nature.

**Sol.** Since no information is given about volume hence we can assume that volume is constant

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

$$\text{given } P_1 = P, \quad T_1 = T, \quad P_2 = P + \frac{0.04P}{100} = 1.004P, \quad T_2 = T + 1$$

$$\therefore \frac{P}{T} = \frac{1.004P}{T+1} \Rightarrow T = 250 \text{ K}$$

$$\text{Final temp.} = 250 + 1 = 251 \text{ K}$$

2. An open vessel at 27°C is heated until 3/5<sup>th</sup> of the air in it has been expelled. Assuming that the volume of the vessel remains constant find

(A) the air escaped out if vessel is heated to 900K.

(B) temperature at which half of the air escapes out.

**Sol.** On heating a gas in a vessel, there are the number of moles of gas which go out, the volume of vessel remains constant.

Let initial no. of moles of gas at 300 K be 'n'. On heating 3/5 moles of air escape out at temperature T.

$$\therefore \text{Moles of air left at temperature } T = \left( n - \frac{3}{5}n \right) = \frac{2n}{5}$$

(A) On heating vessel to 900 K, let  $n_1$  moles be left,

$$n_1 T_1 = n_2 T_2 \Rightarrow n_1 \times 900 = 300 \times n \Rightarrow n_1 = \frac{1}{3}n$$

$$\therefore \text{moles escaped out} = n - \frac{n}{3} = \frac{2}{3}n \text{ moles}$$

(B) Let  $n/2$  moles escape out at temperature T, then

$$n_1 T_1 = n_2 T_2 \Rightarrow \frac{n}{2} \times T = n \times 300 \Rightarrow T = 600 \text{ K}$$

3. When 3.2 g of sulphur is vapourised at 450°C and 723 mm pressure, the vapours occupy a volume of 780 ml. What is the molecular formula of sulphur vapours under these conditions? Calculate the vapour density also.

$$\text{Sol. } PV = nRT \Rightarrow \frac{723}{760} \times \frac{780}{1000} = \frac{3.2}{M} \times 0.082 \times 723$$

$$M = 255.9$$

$$\text{no. of atoms of sulphur in one molecule} = \frac{M}{32} = 8$$

$$\therefore \text{Molecular formula of sulphur} = S_8$$

$$V.D. = \frac{M}{2} = \frac{255.9}{2} \Rightarrow 127.99$$

**Exercise**

5g of ethane is confined in a bulb of one litre capacity. The bulb is so weak that it will burst if the pressure exceeds 10 atm. At what temperature will the pressure of gas reach the bursting value?

**Ans.** 457.81°C

**7. DALTON'S LAW OF PARTIAL PRESSURES**

Dalton's law of partial pressure states "at a given temperature, the total pressure exerted by two or more non reacting gases occupying a definite volume is equal to the sum of the partial pressures of the component gases."

$$P_{\text{total}} = p_1 + p_2 + p_3 + \dots (\text{at constant } V \text{ and } T)$$

$$= \left( \frac{n_1}{V} + \frac{n_2}{V} + \frac{n_3}{V} + \dots \right) RT = (n_1 + n_2 + n_3 + \dots) \frac{RT}{V} = \frac{nRT}{V}$$

where  $n = n_1 + n_2 + n_3 + \dots$  = Total moles,  $V$  = Total volume

$$P_{\text{Total}} = \sum p_i = \frac{RT}{V} \sum n_i$$

If the two non-reacting gases A and B having  $n_A$  and  $n_B$  number of moles respectively are filled in a vessels of volume  $V$  at temperature  $T$ . Then

$$PV = (n_A + n_B)RT \quad \dots(1)$$

Partial pressure may be calculated as

$$p_A V = n_A RT$$

$$p_B V = n_B RT$$

$$\text{Total pressure } (p_A + p_B)V = (n_A + n_B)RT \quad \dots(2)$$

From (1) and (2)

$$P = p_A + p_B$$

$$\frac{p_A}{P} = \frac{\frac{n_A RT}{V}}{(n_A + n_B)RT/V} = \frac{n_A}{n_A + n_B} = x_A \text{ (mole fraction of A)}$$

$$p_A = x_A \times P, \text{ similarly } p_B = x_B \times P$$

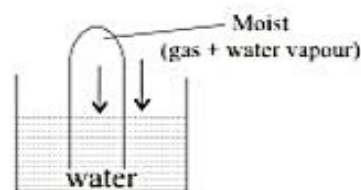
Partial pressure of a component = mole fraction  $\times$  total pressure.

It has been observed that gases are generally collected over water and therefore are moist.

$$P_{\text{dry gas}} = P_{\text{moist gas}} - P_{\text{water vapour}}$$

The pressure exerted by water vapour is constant with water at a particular temperature is called as aqueous tension, which varies directly with the temperature and becomes 760 mm at 100°C

$$\text{Relative Humidity (RH)} = \frac{\text{Partial pressure of water in air}}{\text{Vapour pressure of water}}$$



Pressure of dry gas = Pressure of moist gas – aqueous tension.

### Illustration

0.333 grams of alcohol displaced in a Victor Meyer apparatus  $171 \text{ cm}^3$  of air measured over water at  $15^\circ\text{C}$ . The barometric pressure was 773 torr. Calculate the molecular weight of alcohol. (Aqueous tension at  $15^\circ\text{C} = 13 \text{ torr}$ .)

(A) 33.34 g/mol. (B) 28.80 g/mol. (C) 46.0 g/mol (D) 13.0 g/mol.

Ans. C

Sol.  $P_{\text{dry gas}} = 773 - 13 = 760 \text{ torr}$

$$= \frac{760}{760} = 1 \text{ atm}$$

$$\therefore PV = nRT$$

$$1 \times \frac{171}{1000} = \frac{0.333}{\text{M.wt.}} \times 0.0821 \times 288$$

$$M = 46 \text{ g/mol}$$

### Exercise

Atmospheric air contains 20%  $\text{O}_2$  and 80%  $\text{N}_2$  by volume and exerts a pressure of 760 mm. Calculate the partial pressure of each gas -

(A) 152 mm, 608 mm

(B) 608 mm, 152 mm

(C) 760 mm both

(D) None of these

Ans. A

## 8. AMAGAT'S LAW OF PARTIAL VOLUME

According to this law at constant temperature and pressure, the total volume of non-reacting gaseous mixture is equal to the sum of partial volumes of each component gas present in mixture.

$$V_T = V_1 + V_2 + V_3 + \dots$$

### Partial volume :

Partial volume of any component is defined as the volume occupied by that particular component measured under the given condition of pressure and temperature.

$$PV = nRT$$

$$V \propto n$$



Let us consider a three non-reacting gases A, B and C are present in a container which have number of moles  $n_A$ ,  $n_B$  and  $n_C$  respectively. For each gas partial volume is

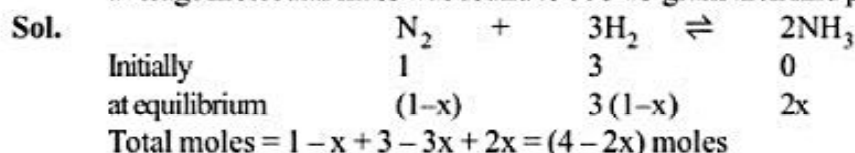
$$V_A = n_A \left( \frac{RT}{P} \right), \quad V_B = n_B \left( \frac{RT}{P} \right) \quad \text{and} \quad V_C = n_C \left( \frac{RT}{P} \right)$$

**Total volume :**

$$V_T = V_A + V_B + V_C = (n_A + n_B + n_C) \left( \frac{RT}{P} \right) = n_T \left( \frac{RT}{P} \right)$$

### Illustration

1. 1 mole of  $N_2$  and 3 moles of  $H_2$  are mixed in 8.21 lit. container at 300 K to form  $NH_3$ . If on equilibrium average molecular mass was found to be  $34/3$  gram then find partial pressure of each component.



Given Average molecular mass =  $\frac{34}{3}$

$$\frac{34}{3} = \frac{28(1-x) + 2(3-3x) + 17(2x)}{(4-2x)} \Rightarrow x = 1/2$$

So total number of moles = 3

$$PV = nRT \Rightarrow P = \frac{nRT}{V} = \frac{3 \times 0.0821 \times 300}{8.21} = 9 \text{ atm}$$

$$p_{N_2} = \frac{1-x}{3} \times P = \frac{0.5}{3} \times 9 = 1.5 \text{ atm}$$

$$p_{NH_3} = \frac{2x \times 9}{3} = \frac{2 \times 0.5 \times 9}{3} = 3$$

$$p_{H_2} = \frac{3-3x}{3} \times P = \frac{1.5}{3} \times 9 = 4.5 \text{ atm}$$

2. At constant temperature of 273 K,  $\frac{1}{V}$  v/s P are plotted for 2 ideal gases A and B as shown. Find out the number of moles of gas A and B.

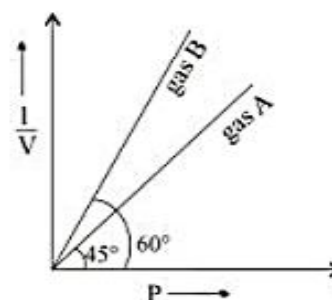
**Sol.**  $PV = nRT, \quad P = \frac{1}{V} nRT$

$$\frac{1}{V} = \frac{1}{nRT} P$$

Comparing by equation :

$$y = mx + C$$

$$C = 0$$



$$m = \frac{1}{nRT} \quad (m = \tan \theta)$$

$$\tan \theta = \frac{1}{nRT} \quad n_A = \frac{1}{RT \tan \theta}$$

$$n_A = \frac{1}{0.0821 \times 273 \times \tan 45^\circ} \Rightarrow n_A = \frac{1}{22.4}$$

$$n_B = \frac{1}{RT \tan 60^\circ} = \frac{1}{22.4\sqrt{3}}$$

### Exercise

1. A vessel of 2 lit. capacity contains hydrogen at 380 mm pressure at 27°C. 16 gm of O<sub>2</sub> is added to the container then find the total pressure (R = 0.0821 L atm mol<sup>-1</sup> K<sup>-1</sup>)
- Ans. 6.65 atm

## 9. GRAHAM'S LAW OF DIFFUSION

Diffusion is the tendency of any substance to spread throughout the space available to it. Diffusion will take place in all direction and even against gravity.

Effusion is the process of gas molecular coming out of container through a small orifice, due to presence difference between container and surrounding atmosphere. The process of effusion is similar to diffusion and same formula are applicable with the only difference that effusion occurs due to presence difference. Effusion always followed by diffusion.

According to Graham, the rate of diffusion (or effusion) of a gas at constant pressure and temperature is inversely proportional to the square root of its molecular mass.

$$r \propto \sqrt{\frac{1}{M}}, \text{ at constant P and T}$$

$$\therefore \frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}, \text{ at constant P and T}$$

Since molecular mass of gas = 2 × vapour density,  $\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}}$ , at constant P and T

The rate of diffusion (or effusion)  $r$  of two gases under different pressure can be given by

$$\frac{r_1}{r_2} = \frac{P_1}{P_2} \times \sqrt{\frac{M_2}{M_1}} \text{ at constant T only.}$$

$$r = \frac{\text{Volume diffused (V)}}{\text{time taken}} = \frac{\text{moles diffused (n)}}{\text{time taken}}$$

$$r = \frac{\text{distance travelled in a narrow tube of uniform cross-sectional area (x)}}{\text{time taken}}$$

Therefore, according to Graham's law of diffusion (effusion) at constant P and T.

$$\frac{V_1}{t_1} \times \frac{t_2}{V_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}}$$

$d_1$  and  $d_2$  are the respective densities and  $V_1$  and  $V_2$  are volumes diffused (effused) in time  $t_1$  and  $t_2$ .

$$\frac{n_1}{t_1} \times \frac{t_2}{n_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}}$$

where  $n_1, n_2$  are moles diffused (effused) in time  $t_1$  and  $t_2$ .

$$\frac{x_1}{t_1} \times \frac{t_2}{x_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}}$$

where  $x_1$  and  $x_2$  are distances travelled by molecules in narrow tube in time  $t_1$  and  $t_2$ .

$$\begin{aligned} r &= \frac{\text{moles diffused}}{\text{time taken}} \\ &= \frac{\text{Distance travelled in a narrow tube}}{\text{time taken}} \\ &= \frac{\text{pressure drop I}}{\text{pressure drop II}} \end{aligned}$$

**Note:** It should be noted that the rate of diffusion or effusion actually depends on pressure difference of the gas and not simply on its pressure. Moreover the pressure difference is to be measured for this gas only i.e. if a container holds [He] at a pressure of 0.1 atm and if a small pin-hole is made in the container and if the container is placed in a room, then the rate of effusion of He gas from the container to outside depends only on its pressure difference, which is 0.1 atm (as there is no He in the atmosphere). This implies that the diffusion of a gas is not dependent on the diffusion of any other gas.

Whenever we consider the diffusion of gas under experimental conditions, we always assume that the gas diffuses in vacuum and during the time period for which the diffusion is studied the rate of diffusion (or the composition of diffusing or effusing mixture of gases) remains constant.

### Application of Graham's law of diffusion in enrichment of isotopes :

#### Enrichment of light component :

If a mixture of heavier gas B and a lighter gas A is placed in contact with a porous barrier, the gas

passing through will be enriched in lighter component by a factor  $\sqrt{\frac{M_B}{M_A}}$ , called enrichment factor

because lighter molecules effuse more rapidly than heavier ones. The remaining gas will be enriched in the heavier component.

Each passage give an enrichment factor equal to  $\sqrt{\frac{M_B}{M_A}}$  and so thousands of such barrier in succession are necessary to provide sufficient enrichment of heavier component.

$$\text{Thus, enrichment factor for first barrier or operation } f_1 = \sqrt{\frac{M_B}{M_A}}$$

$$\therefore \text{ overall separation or enrichment factor } f = \frac{n'_A / n'_B}{n_A / n_B}$$

Where  $n_A$ ,  $n_B$  and  $n'_A$ ,  $n'_B$  are the concentration of two isotopically different components before and after processing. If required enrichment of gas A is attained in x-operation then,

$$(f_1)^x = \frac{n'_A / n'_B}{n_A / n_B} = f$$

$$\text{or } x \log f_1 = \log \left[ \frac{n'_A / n'_B}{n_A / n_B} \right]$$

$$\text{or } x \log \left[ \frac{M_B}{M_A} \right]^{1/2} = \log \left[ \frac{n'_A / n'_B}{n_A / n_B} \right]$$

$$\text{or } \frac{x}{2} \log \left[ \frac{M_B}{M_A} \right] = \log \left[ \frac{n'_A / n'_B}{n_A / n_B} \right]$$

$$\text{or } x = \frac{2 \log \left( \frac{n'_A / n'_B}{n_A / n_B} \right)}{\log \left( \frac{M_B}{M_A} \right)}$$

#### Limitations

- (i) The laws of diffusion and effusion are applicable only when the pressure difference is very small.
- (ii) Correctly speaking the rate of diffusion and effusion are not constant throughout the time interval, but these rates may be assumed constant for a small time interval.



**Illustration**

1. The pressure in a bulb dropped from 2000 to 1500 mm of mercury in 47 minutes when the contained oxygen leaked through a small hole. The bulb was then completely evacuated. A mixture of oxygen and another gas of molecular weight 79 in the molar ratio of 1 : 1 at a total pressure of 4000 mm of mercury was introduced. Find the molar ratio of the two gases remaining in the bulb after a period of 74 minutes.
- Sol.** The molar ratio of oxygen and the other gas in the evacuated bulb = 1 : 1 and the total pressure of the gas mixture is 4000 mm, hence the partial pressure of each gas is 2000 mm.

The drop in the pressure of oxygen after 74 minutes

$$= \frac{(2000 - 1500) \times 74}{47} = 787.2 \text{ mm of Hg}$$

$\therefore$  After 74 minutes, the pressure of oxygen =  $2000 - 787.2 = 1212.8$  mm of Hg

Let the rate of diffusion of other gas be  $r_n$ , then  $\frac{r_n}{r_{O_2}} = \sqrt{\frac{32}{79}}$

$\therefore$  Drop in pressure for the other gas =  $787.2 \times \sqrt{\frac{32}{79}} = 501.01$  mm of Hg

$\therefore$  Pressure of the other gas after 74 minutes =  $2000 - 501.01$  mm of Hg

$$\text{Molar ratio} = \frac{\text{Moles of unknown gas}}{\text{Moles of } O_2} = \frac{1498.99}{1212.8} = 1.236 : 1$$

2. Pure  $O_2$  diffuses through an aperture in 224 seconds, whereas mixture of  $O_2$  and another gas containing 80%  $O_2$  diffuses from the same in 234 sec under similar condition of pressure and temperature. What is molecular wt. of gas?

**Sol.** The gaseous mixture contains 80%  $O_2$  and 20% gas.

$$\therefore \text{Average molecular weight of mixture } (M_{\text{mix}}) = \frac{32 \times 80 + 20 \times m_{\text{mix}}}{100} \quad \dots (i)$$

Now for diffusion of gaseous mixture and pure  $O_2$

$$\frac{r_{O_2}}{r_m} = \sqrt{\frac{M_{\text{mix}}}{M_{O_2}}} \quad \text{or} \quad \frac{V_{O_2}}{V_{\text{mix}}} \times \frac{t_{\text{mix}}}{t_{O_2}} = \sqrt{\frac{M_{\text{mix}}}{32}}$$

$$\text{or} \quad \frac{1}{224} \times \frac{234}{1} = \sqrt{\frac{M_{\text{mix}}}{32}} \quad \dots (ii)$$

$$\therefore M_{\text{mix}} = 34.92$$

By (i) and (ii) mol weight of gas (m) = 46.6.

**Exercise**

Calculate the relative rates of diffusion of  $^{235}\text{UF}_6$  and  $^{238}\text{UF}_6$  in the gaseous state (Atomic mass of F = 19).

Ans. 1.0012

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## 10. CONNECTING CONTAINERS

- (1) When we are connecting two or more containers then the movement of any component of gas occurs in other container till the final pressure of the component in all the container become equal (that means partial pressure becomes equal)
- (2) To calculate composition of gaseous mixture in any container, we will use diffusion.

### Illustration

1. A 10 litre container of 1 mole of gas at 300 K. It is connected to another container having volume 40 litre and is initially at 300K. The nozzle connecting two containers is opened for a long time and once the movement of gas stopped, the larger container was heated to a temperature of 600 K. Calculate
  - (a) Moles and pressure of gas in both the containers before heating.
  - (b) Moles and pressure in two containers after heating. (Assume that initially the larger, container is completely evacuated)

**Sol.** (a) Before heating :

$$PV = nRT$$

$$\frac{(1-x)R \times 300}{10} = \frac{x \times R \times 300}{40}$$

$$x = 0.8 \text{ moles}$$

$$\text{Pressure} = \frac{x \times R \times T}{V} = \frac{0.8 \times R \times 300}{40} = 0.492 \text{ atm}$$

(b) After heating :

$$\frac{(1-x_1)R \times 300}{10} = \frac{x_1 \times R \times 600}{40}$$

$$x_1 = 0.67 \text{ moles, Given } T_1 = 600 \text{ K}$$

$$\text{Pressure} = \frac{x_1 \times R \times T_1}{V} = \frac{0.67 \times 0.0821 \times 600}{40} = 0.821 \text{ atm}$$

### Exercise

1. A mixture containing 1.12 litre  $D_2$  and 2.24 litre of  $H_2$  at NTP is taken inside a bulb connected to another bulb through a stop cock with a small opening. The second bulb is fully evacuated. The stop cock is opened for a certain time and then closed. The first bulb is now found to contain 0.10 g of  $D_2$ . Determine the % by weight of the gases in second bulb.

**Sol.** 41.66 %, 58.33%

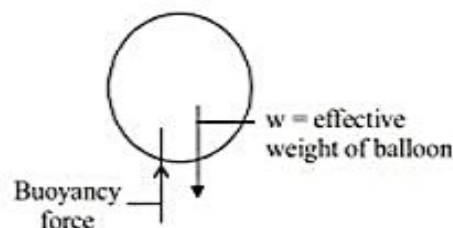
## 11. PAYLOAD OF BALLOON

Payload of a balloon is defined as maximum weight which a balloon can carry with it upward direction.

$V$  = Volume of Balloon,  $d_{air}$  = density of outside air

$d_m$  = density of gas inside,  $m$  = mass of balloon

$$\text{Payload} = d_{\text{out}} \times V \times g - [d_{\text{in}} V \times g + mg] \\ = [\text{Buoyancy force}] - [\text{effective wt. of balloon}]$$



### Illustration

1. Calculate the payload of balloon of diameter 20 meter & weight 100 kg. If it is filled with He at 1.0 atm and 27°C. Density of air is  $1.2 \text{ kgm}^{-3}$ . [ $R = 0.082 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$ ]

Sol. Weight of balloon =  $100 \text{ kg} = 10 \times 10^4 \text{ g}$

$$\text{Volume of balloon} = \frac{4}{3} \pi r^3 = \frac{4}{3} \times \frac{22}{7} \times \left(\frac{20}{2} \times 100\right)^3 \\ = 4190 \times 10^6 \text{ cm}^3 = 4190 \times 10^3 \text{ litre}$$

$$\text{weight of gas (He) in balloon} = \frac{PV}{RT} = \frac{1 \times 4190 \times 10^3 \times 4}{0.082 \times 300} = 68.13 \times 10^4 \text{ g}$$

$$\text{Total weight of gas and balloon} = 68.13 \times 10^4 + 10 \times 10^4 = 78.13 \times 10^4 \text{ g}$$

$$\text{Weight of air displaced} = \frac{1.2 \times 4190 \times 10^6}{10^3} = 502.8 \times 10^4 \text{ g}$$

$$\therefore \text{Payload} = \text{wt. of air displaced} - (\text{wt. of balloon} + \text{wt. of gas})$$

$$\therefore \text{Payload} = 502.8 \times 10^4 - 78.13 \times 10^4 = 424 \times 10^4 \text{ g} = 4.2467 \times 10^6 \text{ g}$$

### Exercise

1. Calculate payload of a balloon having volume 100 litre. It is filled with helium gas at 0.2486 atm pressure and 300K. Density of air is 1.3 gm/litre and mass of material of balloon is 20 gm.

Ans. 1060

## 12. KINETIC THEORY OF GASES

The theoretical model for all the experimental gas laws can be analysed with the help of kinetic theory of gases which is based on following assumptions:

- All the gases consist of very small molecules or atoms whose volume is negligible compared to volume of container.
- There is no interaction between gaseous particles (the interaction may appreciably be affected under certain conditions of temperature and pressure).
- The gaseous molecules are under a state of continuous motion which is unaffected by gravity (the random straight line motion is known as brownian motion).
- Due to the continuous motion, collision between gaseous molecules with the wall of container occurs.

The collision with the wall of container are responsible for pressure exerted by the gas on the wall of container.



- (e) The molecule moves with different speed.  
 (f) All the collision occurring are considered to be perfectly elastic which implies that there is no loss of energy.  
 (g) The average kinetic energy of gas will depends on absolute temperature only.

### 12.1 Equation for kinetic molecular theory

Pressure due to collisions of  $N_0$  molecules on six faces of a cube =  $\frac{1}{3} mN_0 U^2$

$$PV = \frac{1}{3} mN_0 U^2 = \frac{1}{3} MU^2$$

$mN_0 = M$  (molar mass)

$N_0 =$  Avogadro's number

$U =$  root mean square velocity ( $U_{rms}$ )

- Translation kinetic energy of n mole

$$\frac{1}{2} Mu^2 = \frac{3}{2} PV = \frac{3}{2} nRT$$

- Average translational kinetic energy per molecule

$$= \frac{3}{2} \frac{RT}{N_0} = \frac{3}{2} KT$$

Where  $K \left( \frac{R}{N_0} \right)$  is called Boltzmann's constant.

Its numerical value is  $1.38 \times 10^{-16} \text{ erg K}^{-1} \text{ molecule}^{-1}$

Thus average K.E. is proportional to absolute temperature.

If  $T = 0 \text{ K}$  (i.e.,  $-273.15^\circ\text{C}$ ), then average KE = 0

Thus absolute zero (0 K) is the temperature at which molecular motion ceases.

### Illustration

1. Calculate the translational kinetic energy for one mole and one molecule of a gas at 300 K.

**Sol.** Translational kinetic energy per mole =  $\frac{3}{2} RT = \frac{3}{2} \times 8.314 \times 300 = 3741.3 \text{ J/mole}$   
 Translational kinetic energy per molecule =  $\frac{3}{2} KT = \frac{3}{2} \times 1.38 \times 10^{-23} = 6.21 \times 10^{-21}$

### Exercise

1. Calculate the translational kinetic energy for one mole and one molecule of a  $\text{O}_2$  at  $227^\circ\text{C}$ .

**Ans.** 6235.5 J/mole,  $1.035 \times 10^{-20}$

### 12.2 Different types of molecular velocities

- (i) **Root mean square velocity ( $U_{rms}$ )**: It is defined as the square root of the mean of the squares of the velocities possessed by all the molecules present in the given sample of gas

$$U_{rms} = \sqrt{\frac{U_1^2 + U_2^2 + \dots + U_N^2}{N}}$$



$$\therefore U_{\text{rms}} (\text{root mean square velocity}) = \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3P}{d}}$$

Where  $d$  is the density.

If  $N_1$  molecules have velocity  $u_1$  and  $N_2$  molecules have velocity  $u_2$ , then

$$U_{\text{rms}} = \sqrt{\frac{N_1 u_1^2 + N_2 u_2^2}{N_1 + N_2}}$$

- (ii) **Average velocity ( $U_{\text{av}}$ ):** It is given by the arithmetic mean of square of the different velocities possessed by the molecules of the gases at a particular temperature.

$$U_{\text{av}} = \frac{U_1 + U_2 + \dots + U_n}{n}$$

$$U_{\text{av}} (\text{average velocity}) = \sqrt{\frac{8RT}{\pi M}}$$

- (iii) **Most probable velocity ( $U_{\text{mp}}$ ):** It is defined as the velocity possessed by the maximum number of molecules of a gas at a given temperature.

$$U_{\text{mp}} (\text{most probable velocity}) = \sqrt{\frac{2RT}{M}}$$

If  $P$  and  $T$  both are given, use equation in terms of temperature i.e. use

$$U_{\text{rms}} = \sqrt{\frac{3RT}{M}} \text{ and not } \sqrt{\frac{3PV}{M}}$$

To have velocity in  $\text{ms}^{-1}$  (MKS) take  $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ,  $M$  in kg.

If density is in  $\text{kg m}^{-3}$  and  $P$  in  $\text{N m}^{-2}$ , velocity will be in  $\text{ms}^{-1}$

Relation between rms velocity, average velocity and most probable velocity.

$$U_{\text{rms}} : U_{\text{av}} : U_{\text{mp}} = \sqrt{\frac{3RT}{M}} : \sqrt{\frac{8RT}{\pi M}} : \sqrt{\frac{2RT}{M}} = \sqrt{3} : \sqrt{\frac{8}{\pi}} : \sqrt{2} = 1.2248 : 1.1284 : 1$$

$$U_{\text{rms}} = 1.2248 U_{\text{mp}}$$

$$U_{\text{av}} = 1.1284 U_{\text{mp}}$$

$$U_{\text{mp}} = 1.0854 U_{\text{av}}$$

**Illustration**

Calculate  $U_{rms}$ ,  $U_{av}$ ,  $U_{mp}$  at 400 K for hydrogen molecule.

**Sol.**  $U_{mp} = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2 \times 8.314 \times 400}{2 \times 10^{-3}}} = 1823.6 \text{ m/s}$

$$U_{av} = 1.128 U_{mp} = 2057.8 \text{ m/s}$$

$$U_{rms} = 1.2248 U_{mp} = 2233.5 \text{ m/s}$$

**Exercise**

Calculate  $U_{rms}$ ,  $U_{av}$ ,  $U_{mp}$  at 600 K for oxygen molecule.

**Ans.**  $U_{mp} = 558.4 \text{ m/s}$

$$U_{av} = 630.0 \text{ m/s}$$

$$U_{rms} = 683.9 \text{ m/s}$$

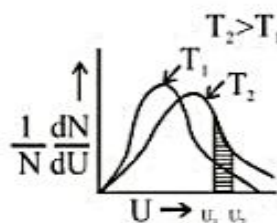
**13. MAXWELL DISTRIBUTION OF MOLECULAR SPEED**

- (a) The speed of a molecule of a gas changes continuously as a result of collisions with other molecules and with the walls of the container. Thus the net result is that we cannot speak of the speed of individual molecule; hence must consider the statistical averages of the speeds of the whole collection of gas molecules.
- (b) The manner in which the molecules of a gas are distributed over the possible speed ranges, from zero to very high values, was first investigated by Maxwell using the theory of probability. His results are expressed as the law of distribution of molecular speeds, one form of which is

$$dN = 4\pi N \left( \frac{m}{2\pi KT} \right)^{3/2} e^{-\frac{mU^2}{2KT}}$$

- (c) The above expression gives the no. of molecules  $dN$  having speeds between  $U$  and  $U + dU$  in terms of total no. of molecules  $N$ , present in the gas.  $m$  is mass of single gas molecule and  $T$  is the absolute temperature of gas.
- (d) The Maxwell distribution of speeds is customarily plotted with the fraction  $\frac{1}{N} \left( \frac{dN}{dU} \right)$  as the ordinate and  $U$  as the abscissa.

$$\frac{1}{N} \frac{dN}{dU} = \frac{1}{dU} \left( \frac{dN}{N} \right)$$



So, the term,  $\frac{1}{N} \frac{dN}{du}$  represents the fraction of molecules in the speed of  $u$  to  $u + du$  per unit interval of speed. Roughly speaking, this gives the probability of finding a molecule with a speed between  $u$  and  $(u + du)$ . The distribution of two temperatures is shown in the fig.

- (e) The curve at any temperature is parabolic near the origin, since the factor  $u^2$  is dominant in this region, the exponential function being approximately equal to unity. At high values of  $u$ , however, the exponential factor dominates the behaviour of the function, causing it to decrease rapidly in value. As a consequence of the contrasting behaviour of two factors, the product function passes through a maximum at a speed known as the most probable speed ( $U_{mps}$ ). Thus, the most probable speed is the speed possessed by the maximum fraction of the molecules.
- (f) It can be seen from the given figure, that the fraction of molecules having either very low speeds or very high speeds are small in numbers. The total area under the curve gives the total no. of molecules in the collection, i.e. the no. of molecules comprising of all speeds. The area under the curve between any two speeds, for example,  $U_1$  and  $U_2$ , gives the total no. of molecules having speed between these two values.
- (g) The given figure illustrates the distribution of speeds at two temperatures  $T_1$  and  $T_2$ . Since the total no. of molecules is the same at both temperatures, increases the K.E. of the molecules, it follows that fraction of molecules having lower speed range decreases on decreasing the temperature whereas fraction of molecules having higher speed range increases on increasing the temperature.
- (h) Also the curve at the higher temperature  $T_2$  has its  $U_{mps}$  shifted to a higher value compared with that for  $T_1$ , whereas corresponding fraction molecules has decreased. But at the same time, the curve near  $U_{mps}$  has become broader at the higher temperature indicating the more molecules possess speeds near to most probable speed.

### Illustration

1. For a sample containing  $O_2$  and  $SO_2$  mark out the **incorrect** statement
  - (A) At same temperature average speed of  $O_2$  is greater than that of  $SO_2$ .
  - (B) If absolute temperature of  $O_2$  is half to that of  $SO_2$  gas than the speed distribution curves will be different.
  - (C) At same temperature & at lower speed, fraction of molecules of  $SO_2$  will be greater.
  - (D) At same temperature & at higher speed, fraction of molecules of  $O_2$  will be greater than that of  $SO_2$ .

Ans. B

Sol.  $M_{O_2} = \frac{1}{2} M_{SO_2}$

$\therefore$  if  $T_{O_2} = \frac{1}{2} T_{SO_2}$

then  $\frac{M_{O_2}}{T_{O_2}} = \frac{M_{SO_2}}{T_{SO_2}}$

$\therefore$  All other parameters are same  $\therefore$  the curves will be same  
option (B)



## Exercise

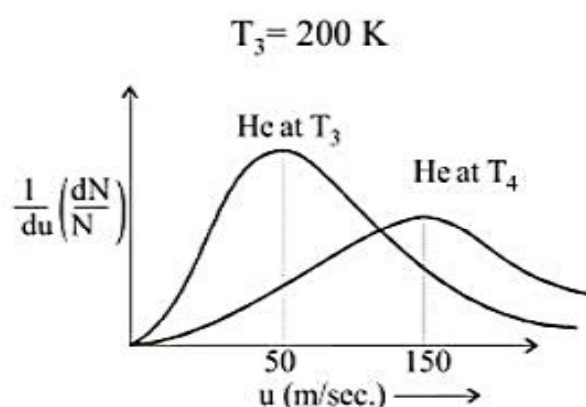
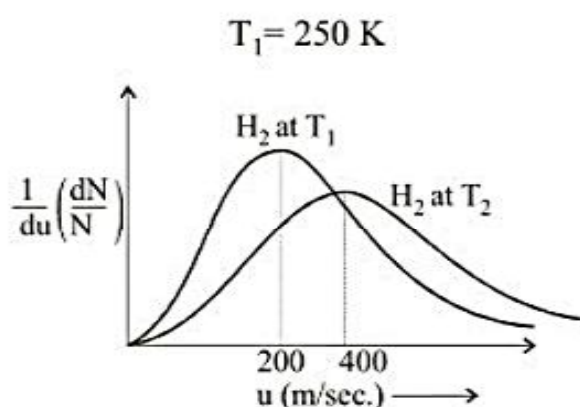
## 1. Find the true /false statement

(A) Most probable speed of ideal gases decreases with increase in molecular mass at constant temperature.

(B) Number of particles moving with most probable speed decreases with increase in molecular mass for ideal gases.

Ans. (A) True (B) False

2.



Select the correct option.

(A)  $U_{mps}$  of  $H_2$  at  $T_2$  is greater than  $U_{mps}$  of He at  $T_4$

(B)  $U_{mps}$  of  $H_2$  at  $T_2$  is less than  $U_{mps}$  of He at  $T_4$

(C)  $U_{mps}$  of  $H_2$  at  $T_2$  is equal to  $U_{mps}$  of He at  $T_4$

(D) None of these

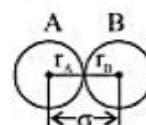
Ans. A

## 14. COLLISION THEORY

## 14.1 Collision diameter :

It is the closest distance between the centres of two molecules taking part in collision.

$$\text{collision diameter } (\sigma) = r_A + r_B$$



## 14.2 Collision Frequency :

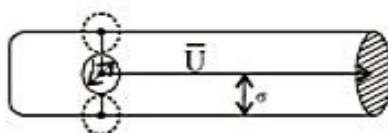
It is the number of molecular collisions taking place per second per unit volume of the gas.

## Determination of number of bimolecular collisions :

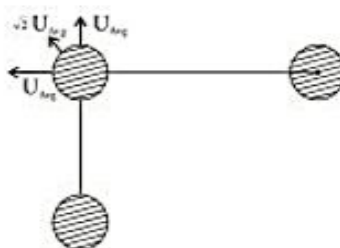
- (a) While considering the molecules among themselves the molecules to be rigid, non-interacting and spherical with diameter  $\sigma$ . It is also assumed that all the molecules move with the same speed. The arithmetic mean of speed is  $U_{Avg}$ .



- (b) Two identical molecules of diameter  $\sigma$  will just touch each other when the distance separating their centres is  $\sigma$ . Thus, a moving molecule will collide with other molecules whose centres come within a distance of  $\sigma$  from its centre. The quantity  $\pi\sigma^2$  is called the collision cross-section for the rigid spherical molecule. It is obvious that this collision cross-section is an area of an imaginary sphere of radius  $\sigma$  around the molecule within which the centre of another molecule cannot penetrate.



- (c) If the molecule is moving with an average speed  $U_{\text{Avg}}$ , then in a unit time area swept out by a single molecule is  $\pi\sigma^2 U_{\text{Avg}}$ . If  $N^*$  is the no. of molecules within the volume ( $N^* = N/V$ ), the no. of collisions by a single molecule in a unit time will be  $\pi\sigma^2 U_{\text{Avg}} N^*$ .
- (d) So, far, we have assumed that only one molecule is moving and all other are stationary. In practice however, this is not true. In order to account for the movements of all molecules, we must consider the average velocity along the line of centre of two colliding molecules instead of average velocity of a single molecule. If it is assumed that, on average, molecules collide while approaching each other perpendicularly, then the average velocity along their centre is  $\sqrt{2} U_{\text{Avg}}$  as shown below.



$\therefore$  The no. of collisions made by a single molecule with other molecules per unit time (collision number) are given by

$$z_1 = \sqrt{2} \pi\sigma^2 U_{\text{Avg}} N^*$$

- (e) The total number of bimolecular collision per unit time is given  $z_{11}$  (collision frequency)

$$\begin{aligned} z_{11} &= \frac{1}{2} (z_1 N^*) = \frac{1}{2} \times N^* \times \sqrt{2} \pi\sigma^2 U_{\text{Avg}} N^* \\ &= \frac{1}{\sqrt{2}} \pi\sigma^2 U_{\text{Avg}} N^{*2} \end{aligned}$$

- (f) If the collisions involve two unlike molecules, the no. of biomolecular collision is given as  $z_{12}$ .

$$z_{12} = \frac{1}{\sqrt{2}} \pi\sigma_{12}^2 U_{12, \text{Avg}} N_1^* N_2^*$$

where  $N_1^*$  and  $N_2^*$  are the no. of molecules per unit volume of the two types of gases,  $\sigma_{12}$  is the average diameter of two molecules, that is

$$\sigma_{12} = \frac{\sigma_1 + \sigma_2}{2} \text{ or } U_{12, \text{Avg}} = [U_{1, \text{Avg}}^2 + U_{2, \text{Avg}}^2]^{1/2}$$

$$U_{1, \text{Avg}}^2 = \frac{8RT}{\pi M_1}, \quad U_{2, \text{Avg}}^2 = \frac{8RT}{\pi M_2}$$

### 14.3 Determination of mean free path and its dependence on pressure and temperature :

- (a) The mean free path is the average distance travelled by a molecule between two successive collision. We can express it as follows :

$$\lambda = \frac{\text{Average distance travelled per unit time}}{\text{No. of collisions made by single molecule per unit time}}$$

$$\lambda = \frac{U_{\text{Avg}}}{z_1} = \frac{U_{\text{Avg}}}{\sqrt{2}\pi\sigma^2 U_{\text{Avg}} N^*} = \frac{1}{\sqrt{2}\pi\sigma^2 N^*}$$

- (b) According to ideal gas equation,

$$PV = nRT = \frac{N}{N_A} RT$$

$$\text{or } P = \left(\frac{N}{V}\right) \left(\frac{R}{N_A}\right) T = \left(\frac{N^*}{V}\right) KT \text{ (where K is known as Boltzmann's constant)}$$

$$\text{Now } \frac{N}{V} = N^*$$

$$\therefore P = N^* KT \text{ or } N^* = \frac{P}{KT} \text{ or } N^* \propto \frac{P}{T}$$

$$(c) \quad \lambda = \frac{1}{\sqrt{2}\pi\sigma^2 N^*}$$

$$\lambda = \frac{1}{N^*} \text{ or } \lambda \propto \frac{1}{N^*}$$

Since, according to gas law  $P \propto T$  at constant volume

$\therefore \lambda = \text{constant at constant volume.}$

Thus there will no effect of changing T or P on  $\lambda$ . If the volume of the gas is kept constant.

$$(d) \quad \text{Now } z_1 = \sqrt{2} \pi \sigma^2 U_{\text{Avg}} N^*$$

$$U_{\text{Avg}} \propto \sqrt{T} \quad \therefore U_{\text{Avg}} = K_1 \sqrt{T}$$

$$N^* \propto \frac{P}{T} \quad \therefore N^* = K_2 \frac{P}{T}$$

$$\therefore z_1 = \sqrt{2} \pi \sigma^2 K_1 K_2 \frac{P}{\sqrt{T}}$$

Now  $z_1 \propto P$  when  $T$  constant

and  $z_1 \propto \frac{1}{\sqrt{T}}$  when pressure is held constant.

At constant volume  $P \propto T$  or  $P = K'' T$

$$\therefore z_1 = \frac{K' K'' T}{\sqrt{T}}$$

or  $z_1 \propto \sqrt{T}$  when volume is constant.

Again  $z_1 \propto \sqrt{P}$  when volume is constant

$$(e) \quad z_{11} = \frac{1}{\sqrt{2}} \pi \sigma^2 U_{\text{Avg}} N^2$$

or  $z_{11} \propto U_{\text{Avg}} N^2$

$$\text{or } z_{11} \propto \sqrt{T} \left( \frac{P}{T} \right)^2$$

$$\text{or } z_{11} \propto \frac{P^2}{T^{3/2}}$$

Thus  $z_{11} \propto P^2$  when temperature is held constant and  $z_{11} \propto T^{-3/2}$  when pressure is held constant

At constant volume

$$z_{11} \propto T^{-1/2} \text{ and } z_{11} \propto P^{1/2}.$$

### Illustration

Calculate the mean free path in  $\text{CO}_2$  at  $27^\circ\text{C}$  and a pressure of  $10^{-9}$  bar. (molecular diameter = 500 pm)

$$[\text{Given : } R = \frac{25}{3} \text{ J mol}^{-1} \text{ K}^{-1}, \sqrt{2} = 1.4, \pi = \frac{22}{7}, N_A = 6 \times 10^{23}]$$

$$\text{Sol. } \lambda = \frac{KT}{\sqrt{2} \pi \sigma^2 P} = \frac{R}{N} \times \frac{T}{\sqrt{2}} \times \pi \sigma^2 P$$

$$= \frac{25}{3} \times \frac{300}{6 \times 10^{23}} \times \frac{7}{1.4 \times 22 \times (500 \times 10^{-10})^2 \times 10^{-9} \times 10^5}$$

$$= 0.0378 \times 10^3 \text{ ms}^{-1}$$

$$= 3.78 \times 10^3 \text{ cms}^{-1}$$



## Exercise

The mean free path of the molecule of a certain gas at 300 K is  $2.0 \times 10^{-5}$  m. The collision diameter of the molecule is 0.2 nm. Calculate

- (a) number of molecules per unit volume of the gas, and  
(b) pressure of the gas

[Given :  $R = \frac{25}{3} \text{ J mol}^{-1} \text{ K}^{-1}$ ,  $\frac{1}{\sqrt{2} \times \pi} = 0.225$ ,  $N_A = 6 \times 10^{23}$ ]

Ans. (a)  $2.81 \times 10^{23} \text{ m}^{-3}$  (b)  $1.17 \times 10^3 \text{ Pa}$

## 15. REAL GAS

Although the ideal gas model is very useful, it is only an approximation of the real nature of gases, and the equations derived from its assumptions ( $PV = nRT$ ) are not entirely dependable. As a consequence, the measured properties of a real gas will often differ from the properties predicted by our calculations. The properties of real gas differ basically of two factors one is force of attraction between molecules and volume of gas molecules.

## 15.1 Difference between real gas &amp; Ideal gas

S.No.	Ideal gas	Real gas
1.	Obeys gas law under all conditions of P and T.	Obeys only at low P and T.
2.	Obeys ideal gas equation	Does not obeys ideal gas equation
3.	Intermolecular interaction between gaseous molecules are negligible.	Intermolecular interaction between gaseous molecules not negligible.
4.	Volume of a particle is negligible as compared to total volume of the gas.	Volume of a particle is not negligible as compared to total volume of the gas
5.	Exists only at high temperature and low pressure	Exists only at low temperature and high pressure

## Explanation of deviation

Kinetic theory of gases do not hold good at all condition mostly these two assumptions

- (a) The force of attraction between gaseous molecules are negligible  
(b) The volume occupied by the gaseous molecules is negligible compared to total volume of gas at high pressure. Both the assumptions do not hold good hence deviating from ideal gas.

## 16. VANDER WAALS EQUATION OF STATE FOR A REAL GAS

The equation of state generated by Vander Waals in 1873 reproduces the observed behaviour with moderate accuracy. For n moles of gas, the Vander Waals equation is

$$\left( P + \frac{n^2 a}{V^2} \right) (V - nb) = nRT$$



where **a** and **b** are constants characteristic of a gas. This equation can be derived by considering a real gas and converting it to an ideal gas.

- 16.1 Volume Correction :** We know that for an ideal gas  $P \times V = nRT$ . Now in a real gas the molecular volume cannot be ignored and therefore let us assume that '**b**' is the volume excluded (out of the volume of container) for the moving gas molecules per mole of a gas. Therefore due to  $n$  moles of a gas the volume excluded would be **nb**.

$\therefore$  a real gas in a container of volume  $V$  has only available volume of  $(V - nb)$  and this can be thought of, as an ideal gas in a container of volume  $(V - nb)$

The Vander Waals constant **b** (the excluded volume) is actually 4 times the volume of a single molecule. i.e.  $b = 4 N_A V$  where  $N_A \rightarrow$  Avogadro number.

$$\therefore b = 4 \times 6.023 \times 10^{23} \times \frac{4}{3} \pi r^3, \text{ where } r \text{ is the radius of a molecule.}$$

- 16.2 Pressure Correction :** Let us assume that the real gas exerts a pressure  $P$ . The molecules that exert the force on the container will get attracted by molecules of the immediate layer which are not assumed to be exerting pressure.

It can be seen that pressure the real gas exerts would be less than the pressure an ideal gas would have exerted. Therefore if a real gas exerts a pressure  $P$ , then an ideal gas would exert a pressure equal to  $P + p$  ( $p$  is the pressure lost by the gas molecules due to attractions). This small pressure  $p$  would be directly proportional to the extent of attraction between the molecules which are hitting the container wall and the molecules which are attracting these.

Therefore  $p \propto \frac{n}{V}$  (concentration of molecules which are hitting the container's wall)

$$p \propto \frac{n}{V} \text{ (concentration of molecules which are attracting these molecules)} \Rightarrow p \propto \frac{n^2}{V^2}$$

$$\therefore p = \frac{an^2}{V^2}$$

where **a** is the constant of proportionality which depends on the nature of gas. Higher value of '**a**' reflects the increased attraction between gas molecules.

- 16.3 The constant a and b:** Vander Waals constant for attraction (**a**) and volume (**b**) are characteristic for a given gas. Some salient features of '**a**' and '**b**' are:

- For a given gas Vander Waal's constant of attraction '**a**' is always greater than Vander Waals constant of volume (**b**).
- The gas having higher value of '**a**' can be liquified easily and therefore  $H_2$  and He are not liquified easily.
- The units of  $a = \text{litre}^2 \text{ atm mole}^{-2}$  and that of  $b = \text{litre mole}^{-1}$
- The numerical values of **a** and **b** are in the order of  $10^{-1}$  to  $10^{-2}$  to  $10^{-4}$  respectively.

**Illustration**

Identify true statement about the vander waal constant 'b' among the statements given below ?

- |   |  |
|---|--|
| I. It is called excluded volume         | II. It accounts for the interparticle forces |
| III. Its units are $\text{mol dm}^{-3}$ | IV. Its value depends on molecular size      |

Ans. I, IV

**Exercise**

Among the four statements given below for real gases, which are correct :

- (A) The molecules causes attractive interactions.  
 (B) They show deviation from ideal gas laws.  
 (C) The molecules are volume less points.  
 (D) The molecules have negligible mass.

Ans. A, B

*Note : The Vander Waal equation can be obtained from ideal gas equation if 'P' is read as pressure exerted when all the intermolecular attractions are removed & 'V' is read as free volume available for the motion of molecules. The inclusions of correction terms, then will give the Vander Waal equation.*

**17. COMPRESSIBILITY FACTOR**

The extent to which a real gas departs from the ideal behaviour may be depicted in terms of a new function called the compressibility factor, denoted by Z. It is defined as

$$Z = \frac{PV}{nRT}$$

The deviations from ideality may be shown by a plot of the compressibility factor Z, against P. For an ideal gas,  $Z = 1$  and it is independent of temperature and pressure.

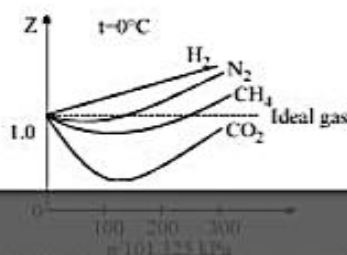
The deviations from ideal behaviour of a real gas will be determined by the value of Z being greater or less than 1.

The difference between unity and the value of the compressibility factor of a gas is a measure of the degree of non ideality of the gas.

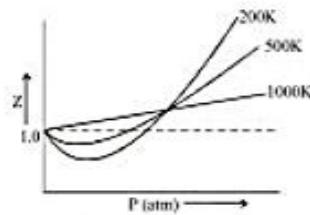
For a real gas, the deviations from ideal behaviour depends on :

- (i) pressure ; and (ii) temperature.

This will be illustrated by examining the compressibility curves of some gases discussed below with the variation of pressure and temperature.

**17.1 Effect of Pressure Variation on Deviations:**

## 17.2 Effect of Temperature on Deviations:



From the above curves we can conclude that:

1. At low pressure and fairly high temperatures, real gases show nearly ideal behaviour and the ideal-gas equation is obeyed.
2. At low temperatures and sufficiently high pressures, a real gas deviates significantly from ideality and the ideal-gas equation is no longer valid.
3. The closer the gas is to the liquefaction point, the larger will be the deviation from the ideal behaviour.

Greater is the departure of  $Z$  from unity, more is the deviation from ideal behaviour.

- (i) When  $Z < 1$ , this implies that gas is more compressible.
- (ii) When  $Z > 1$ , this means that gas is less compressible.
- (iii) When  $Z = 1$ , the gas is ideal.

## 17.3 Explanation of deviation by Van der Waals equation

- (i) **At lower pressure :** ' $V$ ' is large and ' $b$ ' is negligible in comparison with  $V$ .  
Then Vander Waals equation reduces to :

$$\left(P + \frac{a}{V^2}\right)V = RT \quad \Rightarrow \quad PV + \frac{a}{V} = RT$$

$$PV = RT - \frac{a}{V} \quad \Rightarrow \quad Z = \frac{PV}{RT} = 1 - \frac{a}{VRT}, \quad z < 1$$

or  $PV < RT$  at low pressure (below Boyle temperature)  
this accounts for the dip in  $PV$  vs  $P$  isotherm at low pressure.

- (ii) **At fairly high pressures :**  $\frac{a}{V^2}$  may be neglected in comparison with  $P$ .

The Vander Waals equation becomes

$$P(V-b) = RT \quad \Rightarrow \quad PV - Pb = RT$$

$$PV = RT + Pb \quad \Rightarrow \quad Z = \frac{PV}{RT} = 1 + \frac{Pb}{RT}, \quad z > 1$$

or  $PV > RT$  at higher pressure (above Boyle temperature)

This accounts for the rising parts of the  $PV$  vs  $P$  isotherm at high pressures.

- (iii) **At very low pressure :**  $V$  becomes so large that both  $b$  and  $\frac{a}{V^2}$  become negligible and the Vander Waals equation reduces to  $PV = RT$

$$Z = \frac{PV}{RT} = 1 + \frac{Pb}{RT} = \frac{a}{V} \quad \text{At extremely low pressure (at Boyle temperature)}$$

This shows why gases approach ideal behaviour at very low pressures.



- (iv) **Hydrogen and Helium** : These are two lightest gases known. Their molecules have very small masses. The attractive forces between such molecules will be extensively small. So  $\frac{a}{V^2}$  is negligible even at ordinary temperatures. Thus  $PV > RT$ .

### Illustration

1. A real gas obeying vander waal equation will resemble ideal gas if the  
 (A) constants a and b are negligibly small (B) a is large and b is small  
 (C) a is small and b is large (D) constant a and b are large

Ans. A

Sol. At negligible small value of a, b, real gas reduces to ideal gas equation

2. The compressibility factor for 1 mole of a van der Waals gas at 0°C and 100 atm pressure is found to be 0.5. Assuming that the volume of a gas molecule is negligible, calculate the van der Waals constant, a.

Sol. For 1 mole of the gas,

$$Z = \frac{pV}{RT} \Rightarrow 0.5 = \frac{100 \times V}{.0821 \times 273}; V = 0.112 \text{ L}$$

Neglecting b, van der Waals equation reduces to  $\left(P + \frac{a}{V^2}\right) V = RT$

$$\text{or } pV + \frac{a}{V} = RT$$

$$\text{or } 100 \times 0.112 + \frac{a}{0.112} = .0821 \times 273$$

$$a = 1.25 \text{ L}^2\text{atm mol}^{-2}$$

### Exercise

1. The compressibility factor of real gas is usually greater than one ( $Z > 1$ ) at high temperature and high pressure. This is because  
 (A) the constant a is negligible while b is not (B) the constant b is negligible while a is not  
 (C) both a and b are negligible (D) both a and b are no negligible

Ans. A

2. The value of vander Waal's constant 'a' for the gases  $O_2$ ,  $N_2$ ,  $NH_3$  and  $CH_4$  are 1.36, 1.39, 4.17 and 2.253  $\text{L}^2\text{atm, m}^{-2}$ , respectively. The gas which can most easily be liquefied is  
 (A)  $O_2$  (B)  $N_2$  (C)  $NH_3$  (D)  $CH_4$

Ans. C

[Hint - Higher the value of a, easier is the liquification process]



## 18. OTHER EQUATIONS FOR REAL GAS

### 1. Dieterici Equation (for $n$ mole of gas)

$$P(V - nb) = nRT e^{-a/VRT}$$

### 2. Berthelot Equation (for $n$ mole of gas)

$$\left(P + \frac{n^2 a}{TV^2}\right)(V - nb) = nRT$$

### 3. Virial Equation Of State (for $n$ mole of gas)

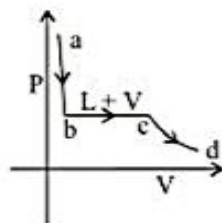
$$Z = \frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \dots$$

$$B = \text{second virial coefficient, temperature dependent} = b - \frac{a}{RT}$$

$$C = \text{third virial coefficient, temperature dependent} = b^2$$

## 19. CRITICAL PHENOMENON & LIQUIFICATION OF GASES

Liquification process is executed by applying pressure at constant temperature and corresponding, a graph is plotted in  $P$  vs  $V$  (called andrew's Isotherm)



L = Liquid phase

V = Vapor phase

a = Initiation of process

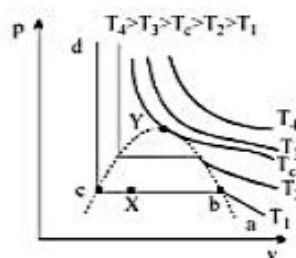
b = start of evaporation

c = End of evaporation

c-d = vapor behaviour

b-c = Constant pressure/constant temp. process

If similar isotherm are plotted at various temperature we get a graph as below.



The phenomena of converting a gas into liquid is known as liquifaction. The liquifaction of gas is achieved by controlling  $P$  and  $T$  as follows :

**19.1 Methods of Liquification of Gases**

- (a) On increasing the pressure gas can be easily liquified because intermolecular attraction between gaseous molecule increases.
- (b) On decreasing the temperature K.E. of gaseous molecules decrease That's why gas can be easily liquified.
- (c) Temperature of gas must be lower than critical temperature ( $T_c$ )

**19.2 Critical temperature ( $T_c$ ) :** It is defined as the characteristic temperature for a given gas below which a continuous increase in pressure will bring liquification of gas and above which no liquefaction is noticed although pressure may be increased e.g.  $T_c$  for  $\text{CO}_2$  is  $31.2^\circ\text{C}$ .

**For a Vanderwaal gas :** 
$$T_c = \frac{8a}{27Rb}$$

**19.3 Critical pressure ( $P_c$ ) :** It is defined as the minimum pressure applied on 1 mole of gas placed at critical temperature, to just liquefy the gas

**For a Vanderwaal gas :** 
$$P_c = \frac{a}{27b^2}$$

**19.4 Critical Volume ( $V_c$ ) :** The volume occupied by 1 mole of gas placed at critical conditions.

**For a Vanderwaal gas :** 
$$V_c = 3b \text{ (i.e. } P = P_c \text{ and } T = T_c \text{)}$$

**19.5 Calculation of critical constants**

$$\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT$$

$$\Rightarrow P V_m - P b + \frac{a}{V_m} - \frac{ab}{V_m} - RT = 0 \quad \text{multiply by } \frac{V_m^2}{P}$$

$$\Rightarrow V - b V_m^2 + \frac{a}{P} V_m - \frac{ab}{P} - \frac{RT}{P} V_m^2 = 0$$

$$\Rightarrow V_m^2 - \left(b + \frac{RT_c}{P_c}\right) V_m + \frac{a}{P_c} - \frac{ab}{P_c} = 0 \dots\dots\dots(1)$$

Again

$$(V_m - V_1)(V_m - V_2)(V_m - V_3) = 0$$

At critical conditions  $V_1 = V_2 = V_3 = V_c$

At critical conditions, gases occupy a definite volume so all the 3 roots will be equal to  $V_c$ .

$$\therefore (V_m - V_c)^3 = 0$$

$$V_m^3 - (3V_c) V_m^2 + (3V_c^2) V_m - V_c^3 = 0 \dots\dots\dots(2)$$

Comparing equation (i) & (ii)

$$3 V_c = b + \frac{RT_c}{p_c} \dots\dots\dots(3)$$

$$3 V_c^2 = \frac{a}{p_c} \dots\dots\dots(4)$$

$$V_c^3 = \frac{ab}{p_c} \dots\dots\dots(5)$$

Dividing (5) equation by (4) equation

$$V_c = 3b$$

$$p_c = \frac{a}{27b^2}$$

$$T_c = \frac{8a}{27Rb}$$

#### Alternative method

- (i) From the graph value of slope at critical conditions is zero

$$\therefore \frac{dP}{dV} = 0$$

- (ii) Before & after the critical point the slope is negative therefore at critical point slope is max.

$$\therefore \frac{d^2P}{dV^2} = 0$$

For 1 mole

$$\left(p + \frac{a}{V_m^2}\right)(V_m - b) = RT$$

$$\Rightarrow P = \left[ \frac{RT}{V_m - b} - \frac{a}{V_m^2} \right] \dots\dots\dots(1)$$

$$\therefore \frac{dp}{dv} = 0 \qquad \therefore RT \frac{d[(v_m - b)^{-1}]}{dv} - \frac{ad[V_m^{-2}]}{dV} = 0$$

$$- \frac{RT}{(v_m - b)^2} + \frac{2a}{v_m^3} = 0 \qquad \dots\dots\dots(2)$$

$$\text{and } \frac{d^2p}{dv^2} = - \frac{2RT}{(v_m - b)^3} - \frac{6a}{v_m^4} = 0 \dots\dots\dots(3)$$

On solving equation (1), (2), (3)

$$V_c = 3b$$

$$p_c = \frac{a}{27b^2}$$

$$T_c = \frac{8a}{27Rb}$$

## 20. BOYLE'S TEMPERATURE

It is the temperature of which a gas behave ideally in a wide range of pressure.

### 20.1 Conversion of Vander Waal's equation in virial form Vander Waal's equation for 1 mole

$$\left( P + \frac{a}{V_m^2} \right) (V_m - b) = RT$$

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

$$\frac{PV_m}{RT} = \left[ \frac{RT}{V_m - b} - \frac{a}{V_m^2} \right] \frac{V_m}{RT}$$

$$Z = \frac{V_m}{V_m - b} - \frac{a}{V_m RT}$$

$$Z = \left( \frac{V_m - b}{V_m} \right)^{-1} - \frac{a}{V_m RT}$$

$$Z = \left[ 1 + \frac{b}{V_m} + \frac{b^2}{V_m^2} + \frac{b^3}{V_m^3} + \dots \right] - \frac{a}{V_m RT}$$

$$Z = 1 + \left( b - \frac{a}{RT} \right) \frac{1}{V_m} + \frac{b^2}{V_m^2} + \frac{b^3}{V_m^3}$$

$$\therefore B = \left( b - \frac{a}{RT} \right); C = b^2; D = b^3$$

### 20.2 For the gas to behave ideally $B = 0$

as the subsequent terms are very small and does not influence much [at low pressure  $P \rightarrow 0$ ]

$$\therefore B = 0$$

$$b - \frac{a}{RT} = 0$$



$$b = \frac{a}{RT}$$

$$T_B = \frac{a}{Rb}$$

Hence it is the temp at which the gas obeys Boyle's law.

### Illustration

The compressibility factor for 1 mole of a Vander Waal's gas at Boyle temperature is

(A)  $1 + \frac{b^2}{V(V-b)}$       (B)  $1 - \frac{b}{V}$       (C)  $1 + \frac{b}{V}$       (D)  $1 - \frac{b^2}{V^2}$

**Ans.** A

**Sol.**  $\left(P + \frac{a}{V^2}\right)(V - b) = RT$

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

$$Z = \frac{PV}{RT} = \frac{V}{V-b} - \frac{a}{VRT}$$

$$= \frac{V}{V-b} - \frac{b}{V} \quad \left(T = \frac{a}{Rb}\right)$$

$$= 1 + \frac{b^2}{V(V-b)}$$

### Exercise

Select correct statement for a real gas.

- (A) Larger the value of  $\frac{T_c}{P_c}$  of gas, larger would be the excluded volume.  
 (B) Critical temperature ( $T_c$ ) of a gas is greater than Boyle's temperature ( $T_b$ )  
 (C) At critical point in the Vander Waal's gas isotherm  $\left(\frac{\partial P}{\partial V}\right)_{T_c} = 0$   
 (D) For a real gas  $T_c = 30^\circ\text{C}$  then it is gas at  $25^\circ\text{C}$  & vapour at  $35^\circ\text{C}$  always.

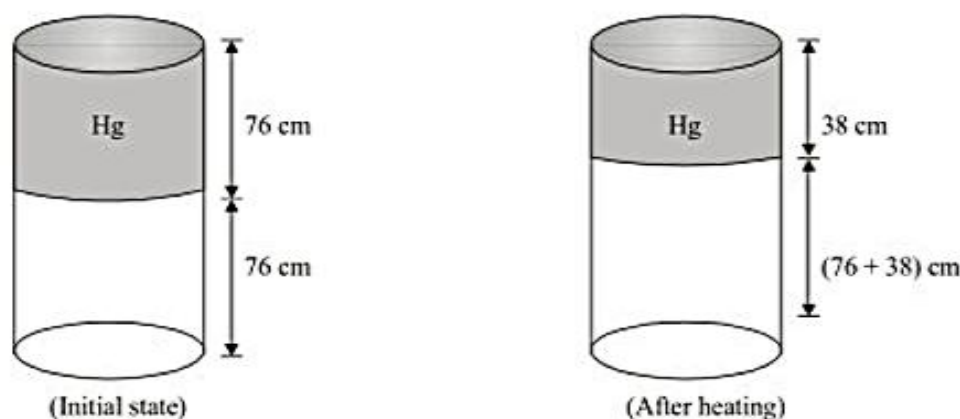
**Ans.** A, C

### SOLVED EXAMPLES

- Q.1** A vertical hollow cylinder of height 1.52 m is fitted with a movable piston of negligible mass and thickness. The lower half of the cylinder contains an ideal gas and the upper half is filled with mercury. The cylinder is initially at 300 K. When the temperature is raised half of the mercury comes out of the cylinder. Find the temperature assuming the thermal expansion of mercury to be negligible.

**Ans.** 337.5 K

**Sol.**



At initial stage :

Pressure of gas = Pressure of Hg + Pressure of atmospheric air

$$= 76 + 76 = 152 \text{ cm}$$

$$T = 300 \text{ K}$$

$$V = \frac{V_1}{2} \text{ where, } V_1 \text{ is volume of cylinder.}$$

At final stage after heating :

Pressure of gas = Pressure of Hg + pressure of atmospheric air

$$= 38 + 76 = 114 \text{ cm}$$

$$V = \frac{3V_1}{4}, T = ?$$

Applying gas equation

$$\frac{152 \times V_1}{2 \times 300} = \frac{114 \times (3V_1 / 4)}{T}$$

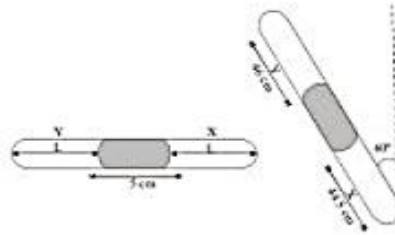
$$T = \frac{114 \times 3 \times 2 \times 300}{4 \times 152} = 337.5 \text{ K}$$

- Q.2** A thin tube of uniform cross-section is sealed at both ends. It lies horizontally, the middle 5 cm containing Hg and the two equal ends containing air at the same pressure  $P_0$ . When the tube is held at an angle  $60^\circ$  with the vertical, the lengths of the air column above and below the mercury are 46 and 44.5 cm respectively.

Calculate pressure  $P_0$  in cm of Hg. (The temperature of the system is kept at  $30^\circ \text{C}$ )

**Ans.** 75.4 cm of Hg

Sol.



At horizontal position, let the length of air column in tube be  $L$  cm.

$$\therefore 2L + 5 = 46 + 5 + 44.5$$

$$L = 45.25 \text{ cm}$$

when the tube is held at  $60^\circ$  with the vertical, the mercury column will slip down.

$$P_Y + 5 \cos 60^\circ = P_X$$

$$P_X - P_Y = \frac{5}{2} = 2.5 \text{ cm Hg} \quad \dots\dots\dots(i)$$

$$\text{From end X, } P_0 \times 45.25 = P_X \times 44.5$$

$$P_X = \frac{45.25}{44.5} P_0 \quad \dots\dots\dots(ii)$$

$$\text{From Y, } P_0 \times 45.25 = P_Y \times 46$$

$$P_Y = \frac{45.25}{46} P_0 \quad \dots\dots\dots(iii)$$

Substituting the values of  $P_X$  and  $P_Y$  in equation (i) we get

$$P_0 = 75.4$$

**Q.3** At fixed temperature and 600 mm pressure, the density of a gas is 42. At the same temperature and 700mm pressure, what is the density of the gas?

**Ans.** 49

**Sol.** According to Boyle's law.

$$P \propto \frac{1}{V} \text{ (at constant temperature)}$$

$$\text{Density } D = \frac{\text{Mass}(M)}{\text{Volume}(V)}$$

$$\text{or } D \propto \frac{1}{V}$$

$$P \propto D$$

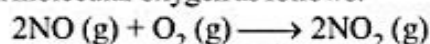
$$\frac{P_1}{D_1} = \frac{P_2}{D_2}$$

$$D_2 = \frac{P_2 \times D_1}{P_1}$$

$$P_1 = 600, D_1 = 42, P_2 = 700$$

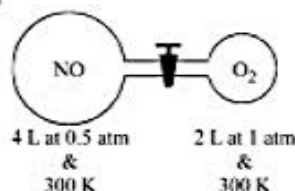
$$D_2 = \frac{700 \times 42}{600} = 49$$

**Q.4** Nitric oxide (NO) reacts with molecular oxygen as follows:



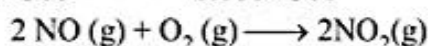
Initially NO & O<sub>2</sub> are separated as shown below. When the valve is opened, the reaction quickly goes to completion. Determine what gases remains at the end of reaction and calculate their partial pressures. Assume that the temperature remains constant at 27°C.

[Given : R = 0.08 atm.L / mole.K]



**Ans.**  $P_{\text{O}_2} = \frac{1}{6} \text{ atm}; P_{\text{NO}_2} = \frac{1}{3} \text{ atm}$

**Sol.** Initially  $n_{\text{NO}} = \frac{0.5 \times 4}{0.080 \times 300}$ ;  $n_{\text{O}_2} = \frac{2 \times 1}{0.080 \times 300}$



Initial  $\frac{2}{24.0} \quad \frac{2}{24.0} \quad 0$

at the end of reaction  $- \quad \frac{1}{24} \quad \frac{2}{24} \Rightarrow \frac{1}{12}$

NO<sub>2</sub> & O<sub>2</sub> gases remains at the end of reactions. **Ans.**

$$V_{\text{total}} = 6 \text{ L}$$

$$\text{P.Pr of O}_2 \Rightarrow \frac{1}{24} \times \frac{0.080 \times 300}{6} \Rightarrow \frac{1}{6} \text{ atm or } 0.166 \text{ atm}$$

$$\text{P.Pr. of NO}_2 \Rightarrow \frac{1}{12} \times \frac{0.080 \times 300}{6} \Rightarrow 0.333 \text{ atm or } \frac{1}{3} \text{ atm}$$

**Q.5** Average velocity of CO<sub>2</sub> at the temperature T<sub>1</sub>K and maximum possible velocity of CO<sub>2</sub> at the temperature T<sub>2</sub> K is  $9 \times 10^{-4} \text{ cm second}^{-1}$  then calculate the value of T<sub>1</sub> and T<sub>2</sub>.

**Ans.** T<sub>1</sub> = 1682.5 K, T<sub>2</sub> = 2143.4 K

**Sol.** Average velocity =  $\sqrt{\frac{8RT}{\pi M}}$

and maximum possible velocity =  $\sqrt{\frac{2RT}{M}}$

Average velocity = Maximum possible velocity =  $9 \times 10^4 \text{ cm sec}^{-1} = 9 \times 10^2 \text{ meter/ second}$

$$\therefore 9 \times 10^2 = \sqrt{\frac{8 \times 8.314 \times T_1}{3.14 \times 44 \times 10^{-3}}}$$

$$9 \times 10^2 = \sqrt{\frac{2 \times 8.314 \times T_2}{44 \times 10^{-3}}}$$

On solving  $T_1 = 1682.5 \text{ K}$

$T_2 = 2143.4 \text{ K}$



**Q.6** Calculate the average kinetic energy of 8 g-molecules of methane at 27°C in Joule.

**Ans.**  $6.21 \times 10^{-21}$  J

**Sol.** Total kinetic energy =  $n\left(\frac{3}{2}RT\right)$

$$\text{Mole number in 8 gram methane} = \frac{8}{16} = 0.5$$

(Molecular weight of methane = 16)

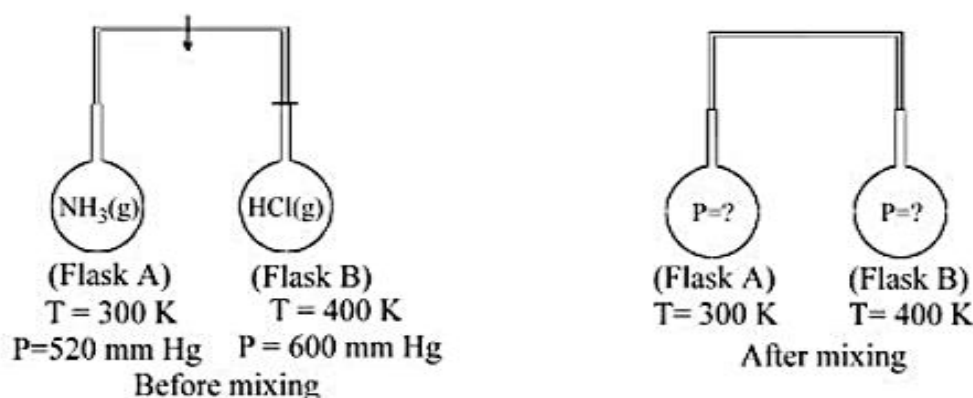
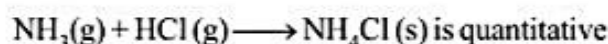
$$R = 8.314 \text{ Joule / K / mole}$$

$$T = 27 + 273 = 300 \text{ K}$$

$$\text{Therefore, kinetic energy} = 0.5 \times \frac{3}{2} \times 8.314 \times 300 = 1870.65 \text{ Joule}$$

$$\therefore \text{Average kinetic energy} = \frac{1870.65}{6.023 \times 10^{23} \times 0.5} = 6.21 \times 10^{-21} \text{ joule}$$

**Q.7** Two flasks A and B of equal volume containing  $\text{NH}_3$  and  $\text{HCl}$  gases, are connected by a narrow tube of negligible volume. The two gases were prevented from mixing by stopper fitted in connecting tube. For further detail of experiment refer to the given figure. What will be final pressure in each flask when passage connecting two tubes are opened. Assume ideal gas behaviour of  $\text{NH}_3$  and  $\text{HCl}$  gas and the reaction.



**Ans.** (A) 40 mm Hg      (B) 60 mm Hg      (C) 20 mm Hg      (D) 10 mm Hg  
(A)

**Sol.**  $P_{\text{HCl}}$  at 300 K =  $\frac{300}{400} \times 600 = 450 \text{ mm Hg}$

Remaining  $P = 520 - 450 = 70 \text{ mm Hg}$   $\text{NH}_3$  in flask 'A'

Let 'x' is numbers of moles of  $\text{NH}_3$  in 'A'

$$\Rightarrow \text{no. of mole of } \text{NH}_3 \text{ in B} = \frac{3}{4}x$$

$$\text{mole fraction of total mole remain in 'A'} = \frac{4}{7}$$

$$\text{Pressure in 'A'} = \frac{4}{7} \times 70 = 40 \text{ mm Hg} \text{ Ans.}$$

**Q.8** The graph of compressibility factor ( $Z$ ) vs  $P$  for one mole of a real gas is shown in following diagram.

The graph is plotted at constant temperature 273 K. If the slope of graph at very high pressure  $\left(\frac{dZ}{dp}\right)$

is  $\frac{1}{10} \text{ atm}^{-1}$ , the volume of one molecule of real gas in  $\text{cm}^3$  is

[Given :  $R = \frac{22.4}{273} \text{ L atm K}^{-1} \text{ mol}^{-1}$  and  $N_A = 6 \times 10^{23}$ ]

(A)  $9.3 \times 10^{-23}$  (B)  $3.7 \times 10^{-20}$  (C)  $9.3 \times 10^{-22}$  (D)  $5.6 \times 10^{-20}$

**Ans.** (C)

**Sol.** At very high pressure

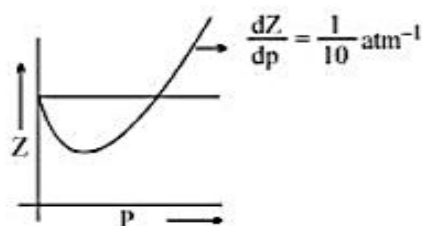
$$Z = 1 + \frac{Pb}{RT}$$

$$\frac{dZ}{dp} = \frac{b}{RT} = \frac{1}{10} \text{ atm}^{-1}$$

$$b = \frac{22.4}{273} \times \frac{273}{10} = 2.24 \text{ litre / mole}$$

$$b = 4 \times V \times N_A$$

$$V = \frac{2.24 \times 10^3}{4 \times 6 \times 10^{23}} \Rightarrow 9.3 \times 10^{-22} \text{ cc} \quad \text{Ans.}$$



**Q.9** The diameters of a bubble at the surface of a lake is 4 mm and at the bottom of the lake is 1 mm. If atmospheric pressure is 1 atm and the temperature of the lake-water and the atmosphere are equal what is the depth of the lake ? (The density of lake-water and Hg are 1 gm/ml and 13.6 respectively. Also neglect the contribution of pressure due to surface tension)

**Ans.** 65116.8 cm

**Sol.** The pressure on the bubble = 1 atm (when it is at the surface)

The pressure on the bubble =  $P$  atm (say) (when it is at the bottom)

$$\text{The volume of the bubble} = \frac{1}{6} \pi (0.1)^3$$

$$P \times \frac{1}{6} \pi \times (1.0)^3 = 1 \times \frac{1}{6} \pi (0.4)^3$$

or  $P = 64 \text{ atm}$ . Thus the pressure due to water is 63 atm ( $\backslash$  atmospheric pressure = 1 atm)

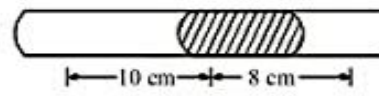
Now, consider the depth of lake is  $h$  cm

$$\therefore 63 \times 76 \times 13.6 \times g = h \times 1 \times g$$

$$\text{or } h = 63 \times 76 \times 13.6 \text{ cm} = 65116.8 \text{ cm.}$$

**Q.10** A 10 cm volume of air is trapped by a column of Hg, 8 cm long in capillary tube horizontally fixed as shown below at 1 atm pressure. Calculate the length of air column when the tube is fixed at same temperature.

- (a) Vertically with open end up  
 (b) Vertically with open end down  
 (c) At  $45^\circ$  from with open end up



(fig. 1)

**Ans.** (a) 9.04 cm (b) 11.18 cm (c) 9.3 cm

**Sol.** (a) When the capillary tube is held as vertically open end up (fig.2),  
 The pressure on the air column = atmospheric pressure + pressure of 8 cm Hg column

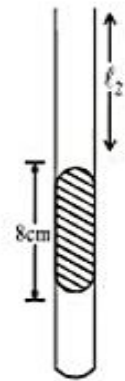
$$= 76 + 8 = 84 \text{ cm of Hg.}$$

Let, at this condition the length of the air column =  $\ell_2$   
 and the length of air column when capillary is horizontally fixed =  $\ell_1 = 10$  cm and pressure on air column = 1 atm.

Let the cross section of the capillary =  $a \text{ cm}^2$

$$\therefore 76 \times 10 \times a = 84 \times \ell_2 \times a$$

$$\text{or } \ell_2 = \frac{76 \times 10}{84} = 9.04 \text{ cm}$$



(fig. 2)

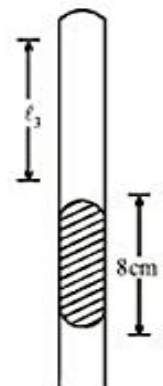
(b) When the capillary tube is held as vertically open end down (fig. 3), the pressure on the air column

$$\begin{aligned} &= \text{atmospheric pressure} - \text{pressure of 8 cm Hg column} \\ &= 76 - 8 = 68 \text{ cm of Hg} \end{aligned}$$

Let at this condition the length of air column =  $\ell_3$ .

$$\therefore 68 \times \ell_3 \times a = 76 \times 10 \times a$$

$$\text{or } \ell_3 = \frac{76 \times 10}{68} = 11.18 \text{ cm}$$



(fig. 3)

(c) When the capillary is held at  $45^\circ$  with open end up, the weight of Hg is partially borne by the gas and partially by the Hg. The pressure on the gas due to Hg column

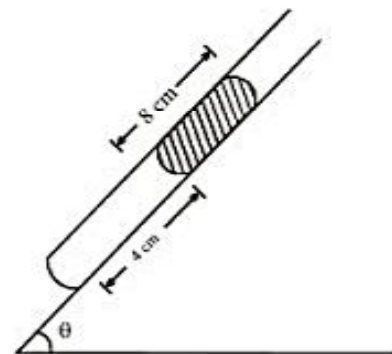
$$= 8 \times \cos 45^\circ$$

$$= 8 \times \frac{1}{\sqrt{2}} = \frac{8}{\sqrt{2}} = \text{cm of Hg}$$

$$\therefore \text{total pressure on the gas} = \left( 76 + \frac{8}{\sqrt{2}} \right) = \text{cm of Hg.}$$

Let length of air column at this pressure =  $\ell_4$ .

$$\therefore \ell_4 \times a \times \left( 76 + \frac{8}{\sqrt{2}} \right) = 10 \times a \times 76$$



(fig. 4)

$$\therefore \ell_4 = \left( \frac{10 \times 76}{76 + 8/\sqrt{2}} \right) = 9.3 \text{ cm}$$

**Q.11** A spherical balloon of 21 cm diameter is to be filled up with hydrogen at NTP from a cylinder containing the gas at 20 atmosphere at 27°C. If the cylinder can hold 2.82 litre of water at NTP, calculate the number of balloon that can be filled up.

**Ans.** 10

**Sol.** Radius of the balloon =  $\frac{21}{2}$  cm = 10.5 cm

$$\text{Volume of the balloon} = \frac{4}{3} \pi r^3 = \frac{4}{3} \times \frac{22}{7} \times (10.5)^3 \text{ cc} = 4851 \text{ cc}$$

$$\text{Pressure} = 1 \times 76 \times 13.6 \times 981 = 1.014 \times 10^6 \text{ dynes/cm}^2$$

$$\therefore \text{No. of mole of H}_2, \text{ the balloon can contain at NTP} = \frac{PV}{RT} = \frac{1.014 \times 10^6 \times 4851}{8.314 \times 10^7 \times 273} = 0.2167$$

$$\text{No. of mole in the cylinder} = \frac{20 \times 76 \times 13.6 \times 981 \times 2820}{8.314 \times 10^7 \times 300} = 2.2929$$

When the balloon are being filled, the pressure in the cylinder will decreases, when the pressure of the cylinder will drop to 1 atm, gas cannot be withdrawn.

$$\text{Now, no. of moles of H}_2 \text{ remaining in the cylinder unused} = \frac{1.014 \times 10^6 \times 2820}{8.314 \times 10^7 \times 300} = 0.1146$$

$$\begin{aligned} \therefore \text{No. of balloon that can be filled} &= \frac{\text{No. of moles of H}_2 \text{ in the cylinder that can be used}}{\text{No. of moles of H}_2 \text{ in one balloon can contain}} \\ &= \frac{2.2929 - 0.1146}{0.2167} = 10 \end{aligned}$$



# ATOMIC STRUCTURE

## 1. INTRODUCTION

**John Dalton** 1808, believed that matter is made up of extremely minute indivisible particles, called **atom** which takes part in chemical reactions. These particle can neither be created nor be destroyed. However, modern researches have conclusively proved that atom is no longer an indivisible particle. Modern structure of atom is based on Rutherford's scattering experiment, quantization of energy and wave mechanical model.

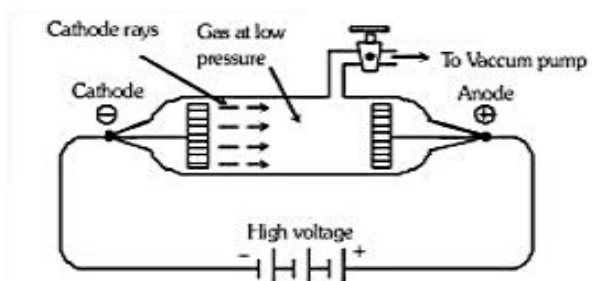
## 2. COMPOSITION OF ATOM

The works of J.J. Thomson and Ernst Rutherford actually laid the foundation of the modern picture of the atom. It is now verified that the atom consists of several sub-atomic particles like electron, proton, neutron, positron, neutrino, meson etc. Out of these particles, the electron, proton and the neutron are called fundamental subatomic particles.

## 3. ELECTRON ( ${}_{-1}e^0$ , $e$ )

3.1 Electron was discovered by **J.J. Thomson (1897)** and it is a negatively charged particle.

3.2 Cathode rays were discovered by **William Crooke & J.J. Thomson** using a cylindrical hard glass tube fitted with two metallic electrodes. This tube was known as discharge tube. They passed electricity (10,000V) through a discharge tube at very low pressure. Blue rays emerged from the cathode. These rays were termed as Cathode rays.



*Discharge tube experiment for production of cathode rays*

### 3.3 Properties of Cathode rays

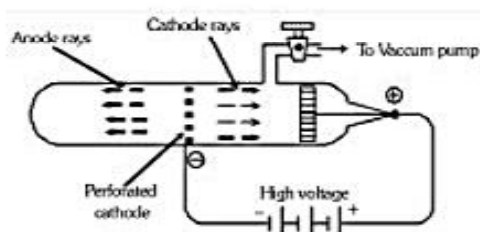
- (i) Cathode rays travel in straight line.
- (ii) Cathode rays produce mechanical effect, as they can rotate the wheel placed in their path.
- (iii) Cathode rays consist of negatively charged particles known as electron.
- (iv) Cathode rays travel with high speed.
- (v) Cathode rays can cause fluorescence.
- (vi) Cathode rays heat the object on which they fall due to transfer of kinetic energy to the object.
- (vii) When cathode rays fall on heavy metals, X-rays are produced.
- (viii) Cathode rays possess ionizing power i.e., they ionize the gas through which they pass.
- (ix) The cathode rays produce scintillation on the photographic plates.
- (x) They can penetrate through thin metallic sheets.
- (xi) The nature of these rays does not depend upon the nature of gas or the cathode material used in discharge tube.

**Note :** The television picture tube is a cathode ray tube in which a picture is produced due to fluorescence on the television screen coated with suitable material. Similarly, fluorescent light tubes are also cathode rays tubes coated inside with suitable materials which produce visible light on being hit with cathode rays.

- 3.4 R.S. Mullikan measured the charge on an electron by oil drop experiment. The charge on each electron is  $-1.602 \times 10^{-19} \text{ C}$ .
- 3.5 The specific charge ( $e/m$ ) on electron was first determined by J.J. Thomson.  
 $e/m = 1.758 \times 10^{-11} \text{ C/kg}$
- 3.6 Rest mass of electron is  $9.109 \times 10^{-31} \text{ kg}$  or, 0.00054 amu

#### 4. PROTON ( ${}_1\text{H}^1$ , $\text{H}^+$ , $\text{P}$ )

- 4.1 Proton was discovered by **Goldstein** and it is positively charged particle. It is a component particle of anode rays. **Goldstein** (1886) used perforated cathode in the discharge tube and repeated cathode rays experiment and observed the formation of anode rays. These rays were also termed as **positive or canal rays**.



*Perforated tube experiment for production of anode rays*

- 4.2 Properties of anode rays
- (i) Anode rays travel in straight line.
  - (ii) Anode rays are material particles.
  - (iii) Anode rays are positively charged.
  - (iv) Anode rays may get deflected by external magnetic field.
  - (v) Anode rays also affect the photographic plate.
  - (vi) The  $e/m$  ratio of these rays is smaller than that of electrons.
  - (vii) Unlike cathode rays, their  $e/m$  value is dependent upon the nature of the gas taken in the tube. It is maximum when gas present in the tube is hydrogen.
  - (viii) These rays produce flashes of light on ZnS screen.
- 4.3 Charge on proton =  $1.602 \times 10^{-19} \text{ coulombs}$
- 4.4 Mass of proton =  $1.673 \times 10^{-27} \text{ kg} = 1.00728 \text{ amu}$
- 4.5 Proton is ionized hydrogen atom  $\text{H}^+$
- 4.6 Specific charge of a proton is  $9.58 \times 10^7 \text{ Coulomb/kg}$

#### 5. NEUTRON ( ${}_0\text{n}^1$ , $\text{n}$ )

- 5.1 Neutron was discovered by James Chadwick (1932) according to the following nuclear reaction,
- $${}_4\text{Be}^9 + {}_2\text{He}^4 \rightarrow {}_6\text{C}^{12} + {}_0\text{n}^1 \text{ or } {}_5\text{B}^{11} + {}_2\text{He}^4 \rightarrow {}_7\text{N}^{14} + {}_0\text{n}^1$$
- 5.2 The reason for the late discovery of neutron was its neutral nature.
- 5.3 Mass of neutron =  $1.675 \times 10^{-27} \text{ kg} = 1.00866 \text{ amu}$
- 5.4 Specific charge of a neutron is zero.
- 5.5 Neutron is fundamental particle of all the atomic nucleus, except hydrogen or protium.

**Illustration**

The mass to charge ratio for  $A^+$  ion is  $1.97 \times 10^{-7} \text{ kg C}^{-1}$ . Calculate the mass of A atom.

Sol. Given  $\frac{m}{e} = 1.97 \times 10^{-7}$

(since  $e = 1.602 \times 10^{-19} \text{ C}$ )

$$\therefore m = 1.97 \times 10^{-7} \times 1.602 \times 10^{-19} \text{ kg}$$

**Exercise**

Arrange the following particles in increasing order of values of  $e/m$  ratio : Electron (e), proton (p), neutron (n) and  $\alpha$ -particle ( $\alpha$ ) -

(A) n, p, e,  $\alpha$

(B) n,  $\alpha$ , p, e

(C) n, p,  $\alpha$ , e

(D) e, p, n,  $\alpha$

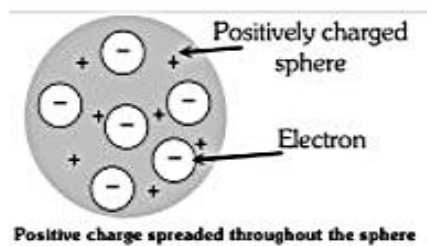
Ans. (B)

**6. THOMSON'S MODEL**

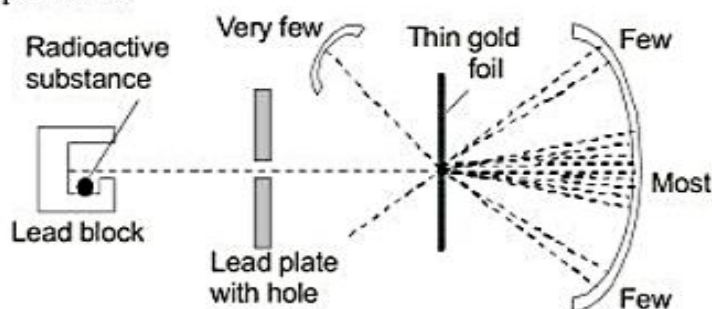
After discovery of electron and proton attempts were made to find out their arrangement in an atom. The first simple model was proposed by J.J. Thomson known as Thomson's atomic model.

He proposed that the positive charge is spread over a sphere of the size of the atom (i.e.  $10^{-8} \text{ cm}$  radius) in which electrons are embedded to make the atom as whole neutral.

This model could not explain the experimental results of Rutherford's  $\alpha$ -particle scattering, therefore it was rejected.

**7. RUTHERFORD'S MODEL**

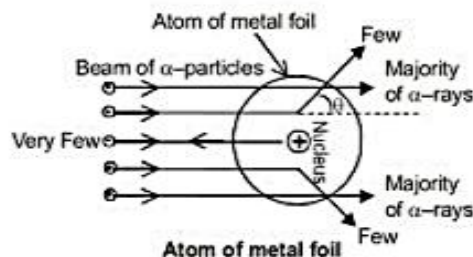
Rutherford carried out  $\alpha$ -particles scattering experiment by the bombardment of high speed  $\alpha$ -particle on thin foil of gold, emitted from radium and gave the following observations, which was based on his experiment.





### 7.1 Observations :

- Most of the  $\alpha$  - particles (nearly 99%) continued with their straight path.
- Some of the  $\alpha$  - particles passed very close to the centre of the atom and deflected by small angles.
- Very few particles thrown back ( $180^\circ$ ).



### 7.2 Main features :

- Most of the  $\alpha$  - particles were continued their straight path that means most of the space inside the atom is empty.
- The centre of an atom has a positively charged body called **nucleus** which repel positively charged  $\alpha$  - particles and thus explained the scattering phenomenon.
- Almost all mass of an atom is concentrated in its nucleus.
- The size and volume of the nucleus is very small as compared to the total size and volume of atom.

### 7.3 Properties of the Nucleus

- Nucleus is a small, heavy, positively charged part of the atom and is located at the centre of the atom.
- All the positive charge of atom (i.e. protons) are present in nucleus.
- Nucleus contains neutrons and protons, and hence these particles collectively are also referred to as nucleons.
- The size of nucleus is measured in Fermi (1 Fermi =  $10^{-13}$  cm =  $10^{-15}$  m). Generally, the radius of the nucleus ( $r_n$ ) is given by the following relation :

$$r_n = r_0 \times A^{1/3}$$

where  $r_0$  is a constant and  $A$  is the mass number.

- The Volume of the nucleus is about  $10^{-45}$  m<sup>3</sup> and that of atom is  $10^{-27}$  m<sup>3</sup>, i.e., volume of the nucleus is  $10^{-15}$  times that of an atom.

**7.4 Distance of closest approach :** When the  $\alpha$ -particle approaches the nucleus to made a head-on collision with a the nucleus, the  $\alpha$ -particle approaches the nucleus until coulombic potential

energy of repulsion,  $k \frac{Z_1 Z_2 e^2}{r}$ , becomes equal to its initial K.E.,  $\frac{1}{2} m.v^2$ .

$$\text{Thus } \frac{1}{2} mv^2 = k \frac{Z_1 Z_2 e^2}{r}$$

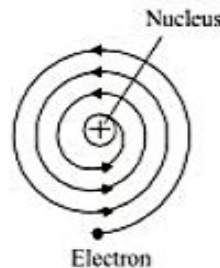
$$\text{Hence, the distance of closest approach, } r = \frac{k Z_1 Z_2 e^2}{\left(\frac{1}{2} mv^2\right)}$$

The nucleus must be further smaller than the distance of closest approach.



### 7.5 Drawbacks of Rutherford's model

- (i) It does not obey the Maxwell theory of electrodynamics. According to this theory a small charged particle moving around an oppositely charged centre continuously loses its energy. If an electron does so, it should also continuously lose its energy and should set up spiral motion ultimately falling into the nucleus.



- (ii) It could not explain the line spectra of atom.

### Illustration

1. Atomic radius is of the order of  $10^{-8}$  cm and nuclear radius is of the order of  $10^{-13}$  cm. Calculate what fraction of atom is occupied by nucleus ?

**Sol.** Volume of nucleus  $= \frac{4}{3} \pi r^3 = \frac{4}{3} \pi (10^{-13})^3 \text{ cm}^3$

Volume of atom  $= \frac{4}{3} \pi (10^{-8})^3 \text{ cm}^3, \quad \frac{V_N}{V_{\text{Atom}}} = \frac{10^{-39}}{10^{-24}} = 10^{-15}$   
 $V_{\text{Nucleus}} = 10^{-15} \times V_{\text{Atom}}$

2. With what velocity should an  $\alpha$ -particle travel towards the nucleus of a Cu atom so as to arrive at a distance  $10^{-13}$  m.

**Sol.**  $\frac{1}{2} m_{\alpha} v_{\alpha}^2 = \frac{k z_1 z_2}{r_{\min}^2} = \frac{k(2e)(63e)}{r_{\min}^2}$

$$v_{\alpha} = \frac{k(2e)(63e)}{m_{\alpha} \cdot r_{\min}^2}$$

$$v_{\alpha} = \sqrt{\frac{2k \cdot 2e \cdot 63e}{m_{\alpha} \cdot r_{\min}^2}} = 6.3 \times 10^6 \text{ m/s}$$

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**Exercise**


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Assuming a spherical shape for fluorine nucleus, calculate the radius and the nuclear density of fluorine nucleus of mass number 19.

**Ans.**  $3.73 \times 10^{-13} \text{ cm}$ ,  $7.616 \times 10^{13} \text{ g cm}^{-3}$

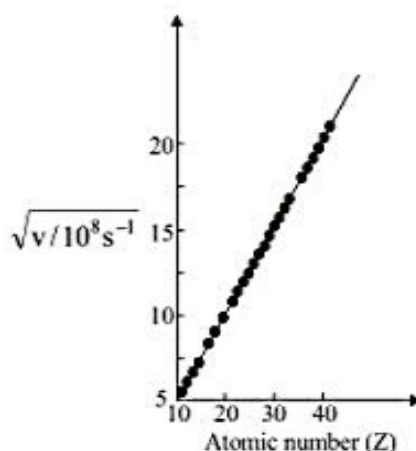
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## 8. MOSELEY EXPERIMENT (DISCOVERY OF ATOMIC NUMBER)

Moseley (1912–1913), investigated the X-rays spectra of 38 different elements, starting from aluminium and ending in gold. He measured the frequency of principal lines of a particular series (the  $\alpha$ -lines in the K series) of the spectra. It was observed that the frequency of a particular spectral line gradually increased with the increase of atomic mass of the element. But, it was soon realised that the frequency of the particular spectral line was more precisely related with the serial number of the element in the periodic table which he termed as atomic number (Z). He presented the following relationship :

$$\sqrt{\nu} = a(Z - b)$$

where,  $\nu$  = frequency of X-rays,  $Z$  = atomic number, 'a' and 'b' are constants. When the values of square root of the frequency were plotted against atomic number of the elements producing X-rays, a straight line was obtained.




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**Illustration**


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If the straight line is at an angle  $45^\circ$  with  $b = 1$  calculate frequency when atomic number  $Z$  is 50.

(A) 2000

(B) 2010

(C) 2401

(D) None

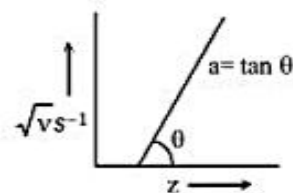
**Ans.** (C)

**Sol.**  $\sqrt{\nu} = \tan 45^\circ = 1 = a$

$$b = 1$$

$$\therefore \sqrt{\nu} = 50 - 1 = 49$$

$$\nu = 2401 \text{ s}^{-1}$$



### Exercise

What is atomic number  $Z$  when  $\nu = 2500 \text{ s}^{-1}$  and value of  $a = 1$  and  $b = 1$

- (A) 50 (B) 40 (C) 51 (D) 53

Ans. (C)

## 9. SOME ATOMIC TERMS

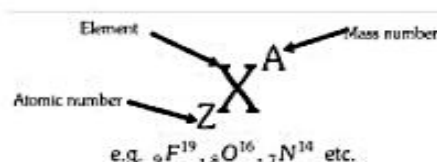
**9.1 Atomic number** = Number of unit positive charge on nucleus = Number of protons in nucleus = Number of electrons in neutral atom.

Two different elements can never have identical atomic number.

**9.2 Mass number (A)** = Number of protons + Number of neutrons or Atomic number (Z)

Hence Number of neutrons =  $A - Z$ .

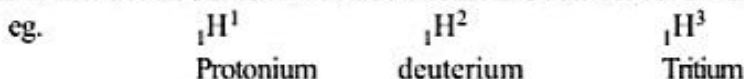
The atom of an element X having mass number (A) and atomic number (Z) may be represented by a symbol,



**9.3** A part of an atom up to penultimate shell is a **kernel** or atomic core.

**9.4** Negative ion (anion) is formed by gaining electrons and positive ion (cation) by the loss of electrons.

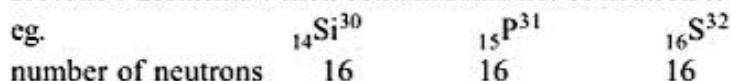
**9.5 Isotopes** : Atoms of an element with the same atomic number but different mass number.



**9.6 Isodiapheres** : The elements which have same value of  $(n - p)$  is called Isodiapheres.



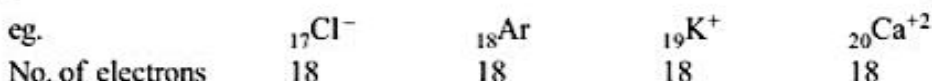
**9.7 Isotone** : Elements which contain same no. of neutron is called **Isotone**.



**9.8 Isobar** : The two different atoms which have same mass number but different atomic number is called Isobar.



**9.9 Isoelectronic** : Ion or atom or molecule which have the same number of electron is called Isoelectronic species.

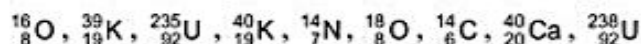


**9.10 Isosters** : Substance which have same number of electrons and the same number of total atoms are called Isosters.



**Illustration**

1. From the following list of atoms, choose the isotopes, isobars and isotones -



**Sol.** Isotopes :  $({}^{16}_8\text{O}, {}^{18}_8\text{O}), ({}^{39}_{19}\text{K}, {}^{40}_{19}\text{K}), ({}^{235}_{92}\text{U}, {}^{238}_{92}\text{U})$

Isobars :  $({}^{40}_{19}\text{K}, {}^{40}_{20}\text{Ca}), ({}^{14}_7\text{N}, {}^{14}_6\text{C})$

Isotones :  $({}^{39}_{19}\text{K}, {}^{40}_{20}\text{Ca}), ({}^{14}_6\text{C}, {}^{16}_8\text{O})$

2. Total number of electrons, protons and neutrons present in the nucleus of  ${}^{238}_{92}\text{U}$  is

(A)  $e = 92, p = 92, n = 146$

(B)  $e = 92, p = 92, n = 148$

(C)  $e = 0, p = 92, n = 146$

(D) None of these

**Ans.** (C)

**Sol.** There is no electron in the nucleus.

$$n_e = 0, n_p = 92, n_n = 238 - 92 = 146$$

**Exercise**

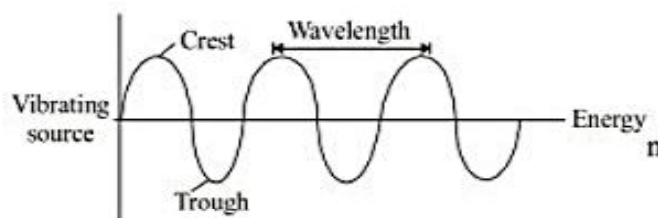
Nitrogen atom has Atomic number 7 & oxygen has Atomic number 8. Calculate the total number of electrons in nitrate ion -

**Ans.** 32

**10. WAVE**

A wave motion is a means of transferring energy from one point to another point without any actual transportation of matter between these points. When we throw a piece of stone on the surface of water in a pond, we observe circles of ever increasing radius, till they strike the wall of the pond. When we put a piece of cork on the surface of this water, we observe that the cork moves up and down as the wave passes, but the piece does not travel along with the waves. The water waves carries the energy but there is no transfer of matter. Thus in a wave motion, disturbance travels through the medium, but the medium does not travel along with the disturbance.

**Some important terms related with wave motion.**



(i) **Wave length ( $\lambda$ )** : The distance between two adjacent crest or trough of the wave (or the distance between two similar neighbouring points)

OR

(ii) **Time period (T)** : Time for one complete oscillation of wave is called the period (T).

Time taken by the wave to travel a distance equal to one wavelength. If C is the

$$\text{speed of wave, then } C = \frac{\lambda}{T}$$



(iii) **Frequency ( $\nu$ )** : Number of oscillations per unit time is called frequency.

$$\nu = \frac{C}{\lambda}$$

(iv) **Wave number ( $\bar{\nu}$ )** : Number of wavelength per unit length.

$$\bar{\nu} = \frac{1}{\lambda}$$

(v) **Amplitude (A)** : It is the height of crest or depth of a trough of a wave.

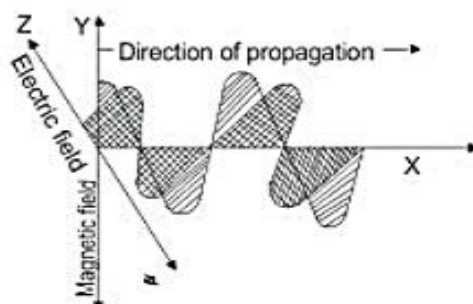
### 10.1 Electromagnetic Wave :

Light is also a type of wave which is known as electromagnetic wave i.e. wave consisting of oscillating electric and magnetic field.

There are various types of electromagnetic waves (radiation) which differs from one another in wavelengths e.g. Visible light, ultraviolet rays, X-rays, infra-red rays, radio waves etc.

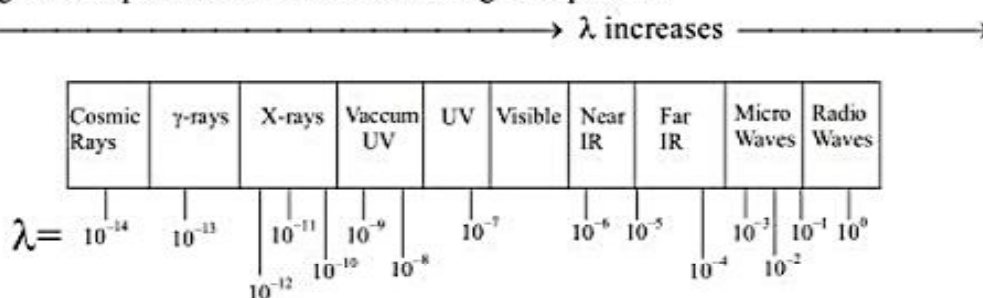
#### Characteristics of electromagnetic radiations:

- All electromagnetic waves move or travel with the same speed equal to that of light.
- They do not require any medium to propagate.
- These consist of electric and magnetic field that oscillate in the direction perpendicular to each other and to the direction in which the wave propagates (as shown in above diagram)



### 10.2 Electromagnetic Spectrum

Arrangement of various types of electromagnetic radiations in order of their increasing (or decreasing) wavelengths or frequencies is known as electromagnetic spectrum.



## 11. SPECTRUM

When light coming from a source is dispersed by a prism, light of different wavelength are deviated through different angles and get separated. This phenomenon is called dispersion and such a dispersed light may be received on a photographic plate or it may be viewed directly by eye. A collection of dispersed light giving its wavelength composition is called a spectrum.

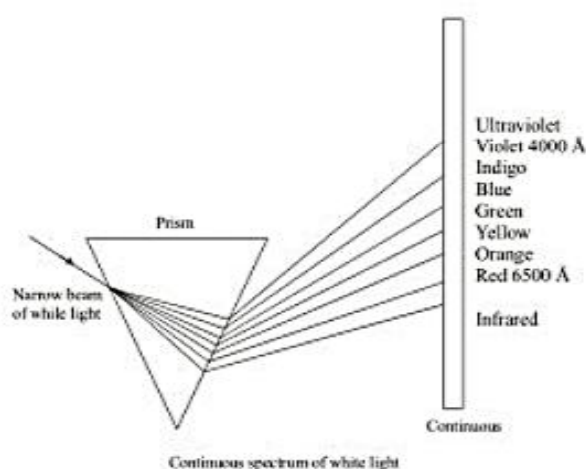
### 11.1 Types of spectrum

1. **Emission spectrum** : A substance gets excited on heating at a very high temperature or by giving energy and subsequently radiations are emitted. These radiations when analysed with the help of spectroscopy, spectral lines are obtained. A substance may be excited-

- (a) By heating at a higher temperature.
- (b) By passing electric current at a very low pressure in a discharge tube filled with a gas.
- (c) By passing electric current into metallic filament.

Emission spectra may be classified as :

- (i) **Continuous spectrum** : When sunlight is passed through a prism, it gets dispersed into continuous bands of different colours. If the light of an incandescent object is resolved through prism or spectroscopy, it also gives continuous spectrum of colours.



- (ii) **Line spectrum** : If the radiations obtained by the excitation of a substance are analysed with the help of a spectroscopy, a series of thin bright lines of specific colours are obtained. There is dark space in between two consecutive lines. This type of spectrum is called line spectrum or atomic spectrum. For example on heating sodium chloride or any other salt of sodium in Bunsen flame bright yellow light is emitted. The emitted light when viewed through a spectroscopy two isolated yellow lines separated by dark space are obtained. The wave lengths of these lines are  $5890\text{\AA}$  and  $5896\text{\AA}$ .

### 2. Absorption spectrum

When the white light of an incandescent substance is passed through any other substance, this substance absorbs the radiations of certain wavelength from the white light. On analysing the transmitted light we obtain a spectrum in which dark lines of specific wave lengths are observed. These lines constitute the absorption spectrum. The wave length of the dark lines correspond to the wavelength of light absorbed.

## 12. MAXWELL THEORY OF ELECTROMAGNETIC WAVE

- (i) All the radiations have wave nature which explains interference (linear superposition) and diffraction.
- (ii) They consist of oscillating electric and magnetic field perpendicular to each other and to the direction of propagation.
- (iii) All the radiations (radio waves, micro waves, infra red waves, visible, UV, X-rays,  $\gamma$ -rays) travel at the speed of light in vacuum.
- (iv) Energy of electromagnetic wave is proportional to amplitude and not linked with frequency of waves.

**Draw backs :** This theory could not explain the following

- (a) Phenomenon of black body radiations (b) Photoelectric effect (c) Line spectra of atoms

### 13. PLANCK'S QUANTUM THEORY

According to this theory atoms or molecules could emit or absorb energy only in discrete quantities (small packets) and not in any arbitrary amount. Planck gave the name quantum to the smallest quantity of energy that can be emitted in the form of E.M. radiation.

The energy of a photon is proportional to its frequency and is given by

$$E = h\nu \text{ where } h = 6.626 \times 10^{-34} \text{ Jsec.}$$

A body can emit or absorb energy only in terms of the integral multiples of quantum, i.e.

$$E = n \cdot h\nu, \text{ where } n = 1, 2, 3, \dots$$

i.e. a body can emit or absorb energy as  $h\nu$ ,  $2h\nu$  ..... but it can not emit or absorb energy in fractional values of  $h\nu$  such as  $1.5 h\nu$ ,  $2.5 h\nu$ .

Einstein supported the planck's theory and explained the photoelectric effect considering that electromagnetic radiations also propagate in the form of photon. Energy of each photon depends on

frequency of light  $\left( E = h\nu = \frac{hc}{\lambda} \right).$

Since wave character of light explains the interference and diffraction phenomenon while the particle character explains, black body radiations and photoelectric effect, the light was considered to have wave as well as particle character [Dual character of light.]

1. Wave nature : diffraction, interference, polarisation.
2. Particle nature : photoelectric effect.

#### Illustration

1. i) What is the energy and wavelength of photons of frequency 3.4 MHz ?  
 ii) Also calculate the energy per mole of photons of the same wavelength.

**Sol.**  $\nu = 3.4 \text{ MHz} = 3.4 \times 10^6 \text{ Hz} = 3.4 \times 10^6 \text{ s}^{-1}$

$$\lambda = \frac{c}{\nu} = \frac{3 \times 10^8 \text{ ms}^{-1}}{3.4 \times 10^6 \text{ s}^{-1}} = 88.2 \text{ m}$$

$$\text{Energy, } E = h\nu = 6.626 \times 10^{-34} \times 3.4 \times 10^6 \text{ J} \\ = 2.253 \times 10^{-27} \text{ J}$$

$$\text{Energy per mole of photon} = 6.02 \times 10^{23} \times 2.53 \times 10^{-27} \text{ J mol}^{-1} \\ = 1.356 \times 10^{-3} \text{ J mol}^{-1}$$

2. The vapours of Hg absorb some electrons accelerated by a potential diff. of 4.5 volt as a result of which light is emitted. If the full energy of single incident  $e^-$  is supposed to be converted into light emitted by single Hg atom, find the wave no. of the light.

**Sol.**  $E = e.V = \frac{hc}{\lambda} \Rightarrow \lambda = \frac{hc}{e.V} = 3.63 \times 10^6 \text{ m}^{-1}$



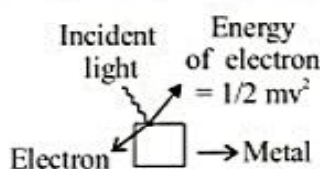
**Exercise**

Calculate the number of photons emitted in 10 hours by a 60 W(J/s<sup>-1</sup>) sodium lamp ( $\lambda$  of photon = 5893 Å)

Ans.  $6.43 \times 10^{24}$

**14. PHOTOELECTRIC EFFECT**

Emission of electrons from a metal surface when exposed to light radiations of appropriate wavelength is called photoelectric effect. The emitted electrons are called **photoelectrons**.



Work function or threshold energy may be defined as the minimum amount of energy required to eject electrons from a metal surface.

According to Einstein,

Maximum kinetic energy of the ejected electron = absorbed energy - work function

$$\frac{1}{2} mv_{\max}^2 = h\nu - h\nu_0 = hc \left[ \frac{1}{\lambda} - \frac{1}{\lambda_0} \right]$$

where,  $\nu_0$  and  $\lambda_0$  are threshold frequency and threshold wavelength respectively.

**Stopping potential** : The minimum potential at which the photoelectric current becomes zero is called stopping potential.

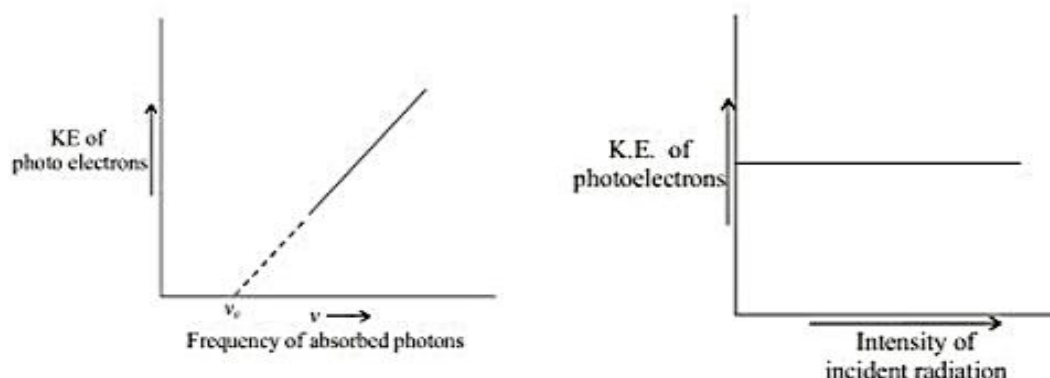
If  $V_0$  is the stopping potential, then

$$eV_0 = h(\nu - \nu_0) \text{ or } V_0 = \frac{h(\nu - \nu_0)}{e} = \frac{\text{K.E.}_{\max.}}{e}$$

**Some facts of Photoelectric Effect**

- (i) There is no time lag between incidence of light and emission of photoelectrons.
- (ii) For emission of photoelectrons, the frequency of incident light must be equal to or greater than the threshold frequency.
- (iii) Rate of emission of photoelectrons from a metal surface is directly proportional to the intensity of incident light.
- (iv) The maximum kinetic energy of photoelectrons depends on the frequency of incident radiation; but, it is independent of the intensity of light used.





### Illustration

1. The minimum energy required to overcome the attractive forces electron and surface of Ag metal is  $7.52 \times 10^{-19}$  J. Calculate the maximum K.E. of electron ejected out from Ag which is being exposed to U.V. light of  $\lambda = 360 \text{ \AA}$

**Sol.**

$$\begin{aligned} \text{Energy absorbed} &= \frac{hc}{\lambda} \\ &= \frac{6.62 \times 10^{-27} \times 3.0 \times 10^{10}}{360 \times 10^{-8}} \\ &= 5.52 \times 10^{-11} \text{ erg} \\ &= 5.52 \times 10^{-18} \text{ Joule} \\ \text{Maximum kinetic energy of electron} &= (7.52 \times 10^{-19}) - (0.552 \times 10^{-19}) \\ &= 6.968 \times 10^{-19} \text{ Joule} \end{aligned}$$

2. A metal was irradiated by light of frequency  $3.2 \times 10^{15} \text{ S}^{-1}$ . The photoelectron produced had its KE, 2 times the KE of the photoelectron which was produced when the same metal was irradiated with a light of frequency  $2.0 \times 10^{15} \text{ S}^{-1}$ . What is work function.

**Sol.**

$$\begin{aligned} E_1 &= h\nu_1 - \phi_0, \quad E_2 = h\nu_2 - \phi_0 \\ \frac{E_1}{E_2} &= \frac{h\nu_1 - \phi_0}{h\nu_2 - \phi_0}, \quad 2 = \frac{h \times 3.2 \times 10^{15} - \phi_0}{h \times 2 \times 10^{15} - \phi_0} \\ \phi_0 &= 319.2 \text{ KJ/Mol} \end{aligned}$$

### Exercise

Light of wavelength  $4000 \text{ \AA}$  falls on the surface of cesium. Calculate the maximum kinetic energy of the photoelectron emitted. The critical wavelength for photoelectric effect in cesium is  $6600 \text{ \AA}$

**Ans.**  $1.95 \times 10^{-19} \text{ Joule}$

## 15. BOHR'S ATOMIC MODEL

This model was based on the quantum theory of radiation and the classical law of physics. It gave new idea of atomic structure in order to explain the stability of the atom and emission of sharp spectral lines.

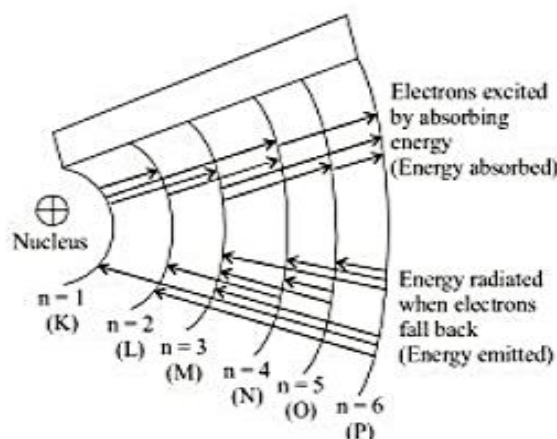
### 15.1 Postulates

- (i) The atom has a central massive core nucleus where all the protons and neutrons are present. The size of the nucleus is very small.
- (ii) The electron in an atom revolve around the nucleus in certain discrete orbits. Such orbits are known as stable orbits or non - radiating or stationary orbits.
- (iii) An electron can move only in those permissive orbits in which the angular momentum ( $mvr$ ) of the electron is an integral multiple of  $h/2\pi$  Thus,

$$mvr = n \frac{h}{2\pi}$$

where,  $m$  = mass of the electron,  $r$  = radius of the electronic orbit,  $v$  = velocity of the electron in its orbit.

- (iv) The angular momentum can be  $\frac{h}{2\pi}, \frac{2h}{2\pi}, \frac{3h}{2\pi}, \dots, \frac{nh}{2\pi}$ . This principal is known as quantization of angular momentum. In the above equation ' $n$ ' is positive integer which has been called as principal quantum number. It can have the values  $n=1, 2, 3, \dots$  (from the nucleus). Various energy levels are designed as  $K(n=1), L(n=2), M(n=3), \dots$  etc. Since the electron present in these orbits is associated with some energy, these orbits are called energy levels.
- (v) The emission or absorption of radiation by the atom takes place when an electron jumps from one stationary orbit to another.



- (vi) The radiation is emitted or absorbed as a single quantum (photon) whose energy is equal to the difference in energy of the electron in the two orbits involved. Thus,  $\Delta E = h\nu$ , where  $h$  = Planck's constant and  $\nu$ , frequency of the radiant energy. Hence the spectrum of the atom will have certain fixed frequency.
- (vii) The lowest energy state ( $n=1$ ) is called the ground state. When an electron absorbs energy, it gets excited and jumps to an outer orbit. It has to fall back to a lower orbit with the release of energy.

### 15.2 Advantage of Bohr's theory

- (i) Bohr's theory satisfactorily explains the spectra of species having one electron, viz. hydrogen atom,  $\text{He}^+, \text{Li}^{2+}$  etc.
- (ii) **Calculation of the radius of the Bohr's orbit:**

Suppose that an electron having mass ' $m$ ' and charge ' $e$ ' revolving around the nucleus of charge ' $Ze$ ' ( $Z$  is atomic number &  $e$  is charge) with a tangential / linear velocity of ' $v$ '. Further consider that ' $r$ ' is the radius of the orbit in which electron is revolving.

According to **Coulomb's law**, the electrostatic force of attraction (F) between the moving electron and nucleus is -

$$F = \frac{KZe^2}{r^2}$$

Where :  $K = \text{constant} = \frac{1}{4\pi\epsilon_0} = 9 \times 10^9 \text{ Nm}^2/\text{C}^2$

and the centripetal force  $F = \frac{mv^2}{r}$

Hence 
$$\frac{mv^2}{r} = \frac{KZe^2}{r^2}$$

$$\text{or, } v^2 = \frac{KZe^2}{mr} \dots(1)$$

From the postulate of Bohr,

$$mvr = \frac{nh}{2\pi}$$

$$\text{or, } v^2 = \frac{n^2h^2}{4\pi^2m^2r^2} \dots(2)$$

From equation (1) and (2) :

$$\therefore r = \frac{n^2h^2}{4\pi^2mKZe^2}$$

On putting the value of e, h, m,

$$r = 0.529 \times \frac{n^2}{Z} \text{ \AA}$$

**(iii) Calculation of velocity of an electron in Bohr's orbit :**

Velocity of the revolving electron in  $n^{\text{th}}$  orbit is given by -

$$mvr = \frac{nh}{2\pi} \quad v = \frac{nh}{2\pi mr}$$

Putting the value of r in above equation

then 
$$v = \frac{nh \times 4\pi^2mZe^2}{2\pi mn^2h^2}$$

$$v = \frac{2\pi Ze^2}{nh}$$

on putting the values of e and h,

$$v = 2.188 \times 10^6 \times \frac{Z}{n} \text{ m/sec}$$

**(iv) Calculation of energy of an electron :**

The total energy of an electron revolving in a particular orbit is -

$$T. E. = K. E. + P. E.$$

$$\text{The K.E. of an electron} = \frac{1}{2}mv^2$$

$$\text{and the P.E. of an electron} = -\frac{kZe^2}{r}$$

$$\text{Hence, } T.E. = \frac{1}{2}mv^2 - \frac{kZe^2}{r} \quad \dots\dots\dots(3)$$

$$\text{But } \frac{mv^2}{r} = \frac{kZe^2}{r^2} \quad \text{or } mv^2 = \frac{kZe^2}{r}$$

Substituting the value of  $mv^2$  in the equation (3)

$$T.E. = \frac{kZe^2}{2r} - \frac{kZe^2}{r} = -\frac{kZe^2}{2r}$$

$$\text{So, } T.E. = -\frac{kZe^2}{2r}$$

Substituting the value of 'r' in the equation of T.E. .

$$E = -\frac{kZe^2}{2} \times \frac{4\pi^2Ze^2mk}{n^2h^2} = -\frac{2\pi^2Z^2e^4mk^2}{n^2h^2}$$

Thus, the total energy of an electron in  $n^{\text{th}}$  orbit is given by

$$\begin{aligned} E_n &= \frac{2\pi^2Z^2e^4mk^2}{n^2h^2} \\ &= -13.6 \times \frac{Z^2}{n^2} \text{ eV / atom} \\ &= -21.8 \times 10^{-19} \times \frac{Z^2}{n^2} \text{ J / atom} \\ &= -313.6 \times \frac{Z^2}{n^2} \text{ Kcal / mole} \end{aligned}$$

**(v) Relation between P. E., K. E. & T. E. :**

$$P. E. = -\frac{kZe^2}{r}, \quad K. E. = \frac{1}{2} \frac{kZe^2}{r}, \quad T. E. = -\frac{1}{2} \frac{kZe^2}{r}$$

$$T.E. = \frac{P.E.}{2} = -K.E.$$

**(vi) Calculation of the number of revolutions of the electron in an orbit per second**

$$\text{Number of revolutions per sec.} = \frac{\text{velocity of the electron}}{\text{Circumference of the orbit}}$$



$$= \frac{v}{2\pi r} = \frac{nh}{2\pi mr} \times \frac{1}{2\pi r} \quad \left[ \text{On substituting the value of } v \text{ from } mvr = \frac{nh}{2\pi} \right]$$

$$= \frac{nh}{4\pi^2 mr^2}$$

$$\text{No. of revolutions per second} = \frac{nh}{4\pi^2 mr^2} = \frac{nh}{4\pi^2 m} \times \left( \frac{4\pi^2 mze^2 k}{n^2 h^2} \right)^2$$

$$= \frac{4\pi^2 mze^4 k^2}{n^3 h^3}$$

$$\text{Time taken for one revolution (Time period)} = \frac{4\pi^2 mr^2}{nh} = \frac{n^3 h^3}{4\pi^2 mze^4 k^2}$$

### Illustration

1. The radius of the an orbit of hydrogen atom is 0.85 nm. Calculate the velocity of electron in this orbit.

Sol.  $r = r_0 n^2 \quad n^2 = 16,$   
 $n = 4$

$$V = V_0 \cdot \frac{Z}{n} = 2.186 \times 10^6 \times \frac{1}{4} = 5.44 \times 10^5 \text{ m/s}$$

2. The energy of an excited H-atom is -3.4 eV. Calculate angular momentum of  $e^-$  in the given orbit.

Sol.  $E = -13.6 \frac{Z^2}{n^2} \Rightarrow n^2 = \frac{13.6}{3.4} = 4$   
 $n = 2$

$$\text{Angular momentum} = mvr = \frac{nh}{2\pi} = \frac{h}{\pi}$$

3. Ionisation energy of hydrogen atom is 13.6 eV. Calculate the ionisation energy for  $\text{Be}^{3+}$  in the first excited state.

Sol. Ionization energy of hydrogen =  $-E_1$  (Energy of first Bohr orbit)

$$\text{I.E.} = -E_1 = -\left(-13.6 \frac{Z^2}{n^2}\right) = +13.6 \times \frac{1^2}{1^2} = 13.6 \text{ eV}$$

Ionization energy of  $\text{Be}^{3+}$

$$Z = 4$$

$n = 2$  (for 1<sup>st</sup> excited state)

$$\text{I.E.} = \left(13.6 \frac{4^2}{2^2}\right) = 54.4 \text{ eV}$$

The ionization energy of H-atom is 13.6 eV. Calculate the ionization energy of  $\text{Li}^{+2}$  ion -

Ans. 122.4 eV

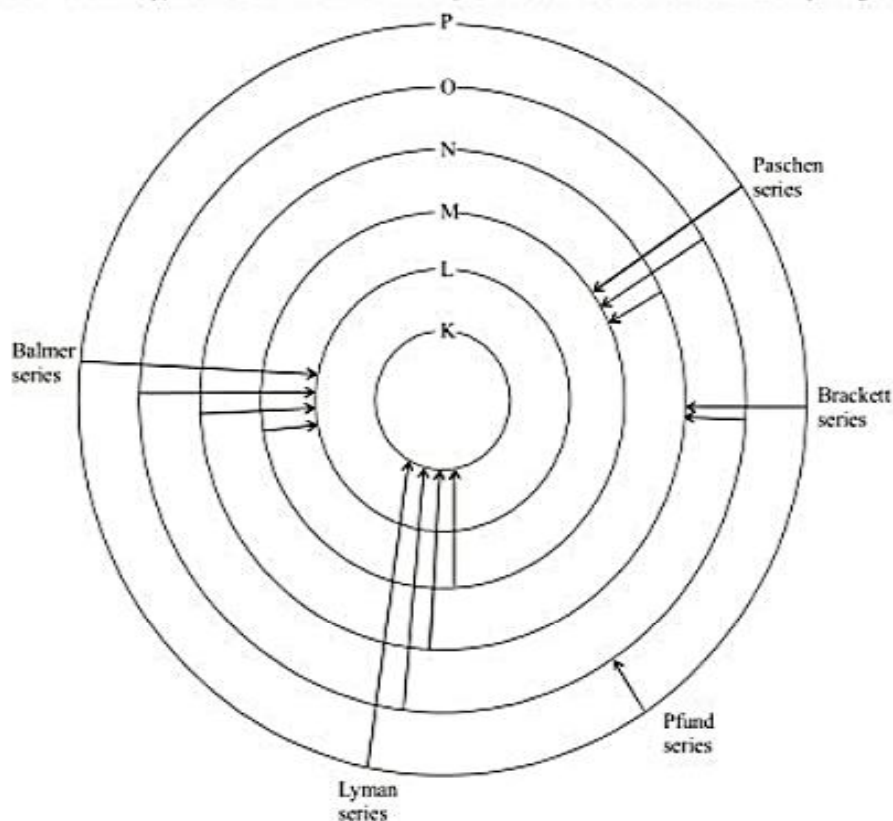
### 15.3 Hydrogen Spectrum

Hydrogen spectrum is an example of line or atomic emission spectrum. When an electric discharge is passed through hydrogen gas at low pressure, a bluish light is emitted. This light shows discontinuous line spectrum of several isolated sharp lines through prism. All these lines of H-spectrum have Lyman, Balmer, Paschen, Brackett, Pfund and Humphrey series. These spectral series were named by the name of scientist discovered them. To evaluate wavelength of various H-lines Rydberg introduced the following expression,

$$\bar{\nu} = \frac{1}{\lambda} = \frac{\nu}{c} = R \left[ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

Where R is a constant known as Rydberg's constant its value is  $109,67800 \text{ m}^{-1}$ .

Although H-atom consists only one electron yet its spectra consist of many spectral lines because electrons in different hydrogen atoms absorb different amount of energies and are excited to different energy levels. Since life time of electrons in these excited states is very small, they return to some lower energy level or even to the ground state in one or more jumps



Maximum number of lines produced when an electron jumps from  $n$ th level to ground level =  $\frac{n(n-1)}{2}$ .

**(A) Lyman Series**

- (a) It is a first series of spectral series of H.
- (b) It was found out in ultraviolet region in 1898 by *Lyman*.
- (c) It's value of  $n_1 = 1$  and  $n_2 = 2, 3, 4$  where ' $n_1$ ' is ground state and ' $n_2$ ' is called excited state of electron present in a H - atom.
- (d) If the electron goes to  $n_1 = 1$  from  $n_2 = 2$  — first Lyman series  
 If the electron goes to  $n_1 = 1$  from  $n_2 = 3$  — Second Lyman series  
 If the electron goes to  $n_1 = 1$  from  $n_2 = 4$  — third Lyman series ----- so on.

(e)  $\frac{1}{\lambda} = R_H \left[ \frac{1}{1^2} - \frac{1}{n_2^2} \right]$  where  $n_2 > 1$  always.

(f) For marginal line or limiting line  $n_2 = \infty$ . Hence the wavelength of marginal line =  $\frac{n_1^2}{R_H}$  for all series.

So, for lyman series it is  $\frac{1}{R_H}$

**(B) Balmer series :**

- (a) It is the second series of H-spectral series.
- (b) It was found out in 1892 in visible region by *Balmer*.
- (c) Balmer series was found out before all series because it was found in visible region.
- (d) It's value of  $n_1 = 2$  and  $n_2 = 3, 4, 5$  .....
- (e) If the electron goes to  $n_1 = 2$  from  $n_2 = 3$  — First Balmer series  
 If the electron goes to  $n_1 = 2$  from  $n_2 = 4$  — Second Balmer series  
 If the electron goes to  $n_1 = 2$  from  $n_2 = 5$  — third Balmer series .... so on

(f) The wavelength of marginal line of Balmer series =  $\frac{n_1^2}{R_H} = \frac{2^2}{R_H} = \frac{4}{R_H}$

(g)  $\frac{1}{\lambda} = R_H \left( \frac{1}{2^2} - \frac{1}{n_2^2} \right)$  where  $n_2 > 2$  always

**(C) Paschen series :**

- (a) It is the third series of H - spectrum.
- (b) It was found out in infra red region by *Paschen*.
- (c) It's value of  $n_1 = 3$  and  $n_2 = 4, 5, 6$  .....
- (d) If the electron goes to  $n_1 = 3$  from  $n_2 = 4$  — First paschen series  
 If the electron goes to  $n_1 = 3$  from  $n_2 = 5$  — second paschen series  
 If the electron goes to  $n_1 = 3$  from  $n_2 = 6$  — third paschen series ----- so on.

(e) The wavelength of marginal line of paschen series =  $\frac{n_1^2}{R_H} = \frac{3^2}{R_H} = \frac{9}{R_H}$ .

(f)  $\frac{1}{\lambda} = R_H \left[ \frac{1}{3^2} - \frac{1}{n_2^2} \right]$  where  $n_2 > 3$  always.

**(D) Brackett series :**

- (a) It is fourth series of H - spectrum.
- (b) It was found out in infra red region by *Brackett*.
- (c) It's value of  $n_1 = 4$  and  $n_2 = 5, 6, 7$  .....

- (d) If the electron goes to  $n_1 = 4$  from  $n_2 = 5$  — first brackett series  
 If the electron goes to  $n_1 = 4$  from  $n_2 = 6$  — second brackett series  
 If the electron goes to  $n_1 = 4$  from  $n_2 = 7$  — third brackett series ----- so on.

(e) The wavelength of marginal line of brackett series =  $\frac{n_1^2}{R_H} = \frac{4^2}{R_H} = \frac{16}{R_H}$

(f)  $\frac{1}{\lambda} = R_H \left[ \frac{1}{4^2} - \frac{1}{n_2^2} \right]$  Where  $n_2 > 4$  always.

**(E) Pfund series :**

- (a) It is fifth series of H - spectrum.  
 (b) It was found out in infra red region by Pfund.  
 (c) It's value of  $n_1 = 5$  and  $n_2 = 6, 7, 8$  .....  
 (d) If the electron goes to  $n_1 = 5$  from  $n_2 = 6$  — first Pfund series  
 If the electron goes to  $n_1 = 5$  from  $n_2 = 7$  — second Pfund series  
 If the electron goes to  $n_1 = 5$  from  $n_2 = 8$  — third Pfund series -----so on.

(e) The wavelength of marginal line of Pfund series =  $\frac{n_1^2}{R_H} = \frac{5^2}{R_H} = \frac{25}{R_H}$

(f)  $\frac{1}{\lambda} = R_H \left[ \frac{1}{5^2} - \frac{1}{n_2^2} \right]$  where  $n_2 > 5$  always.

**(F) Humfrey series :**

- (a) It is the sixth series of H - spectrum.  
 (b) It was found out in infra-red region by *Humfrey*.  
 (c) It's value of  $n_1 = 6$  and  $n_2 = 7, 8, 9$  .....  
 (d) If the electron goes to  $n_1 = 6$  from  $n_2 = 7$  — first Humfrey series  
 If the electron goes to  $n_1 = 6$  from  $n_2 = 8$  — second Humfrey series  
 If the electron goes to  $n_1 = 6$  from  $n_2 = 9$  — third Humfrey series ... so on.

(e) The wavelength of marginal line of Humfrey series =  $\frac{n_1^2}{R_H} = \frac{6^2}{R_H} = \frac{36}{R_H}$

(f)  $\frac{1}{\lambda} = R_H \left[ \frac{1}{6^2} - \frac{1}{n_2^2} \right]$  where  $n_2 > 6$ .

**Note :**  $\alpha$  - line = first line of series.

Similarly  $\beta$ -line = second line of series

For example : First line ( $\alpha$ -line) of Paschen series will be from  $n_2 = 4$  to  $n_1 = 3$

#### 15.4 Calculation of Rydberg Constant from bohr's atomic model

Suppose that an electron transist from first energy level to second energy level. Then, the change of energy is given by

$$\Delta E = E_{n_2} - E_{n_1}$$



$$\text{or, } = \left[ \frac{-2\pi^2 m Z^2 e^4 k^2}{n_2^2 h^2} \right] - \left[ \frac{-2\pi^2 m Z^2 e^4 k^2}{n_1^2 h^2} \right] \quad \text{or, } \frac{hc}{\lambda} = \frac{-2\pi^2 m Z^2 e^4 k^2}{h^2} \times \left[ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

$$\text{or, } \frac{1}{\lambda} = \frac{2\pi^2 m Z^2 e^4 k^2}{ch^3} \left[ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right] = R_H \cdot Z^2 \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$\text{or, } R_H = \frac{2\pi^2 m e^4 k^2}{ch^3} = \text{Rydberg constant}$$

### Illustration

1. Calculate the wavelength of radiation emitted, producing a line in Lyman series, when an electron falls from fourth stationary state in hydrogen atom.

Sol.  $\frac{1}{\lambda} = RZ^2 \left[ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$

$$\frac{1}{\lambda} = R \left[ \frac{1}{1^2} - \frac{1}{4^2} \right] \quad (\text{For H-atom, } Z = 1, \text{ Lyman series; } n_1 = 1)$$

$$\lambda = 9.7 \times 10^{-8} \text{ m}$$

2. Calculate the wave no. for the shortest wavelength transition in the Balmer series of atomic hydrogen.

Sol. For shortest wavelength  $n_2 \rightarrow \infty$

$$\bar{\nu} = R \left[ \frac{1}{2^2} - \frac{1}{\infty^2} \right] = \frac{R}{4} = 27419.25 \text{ cm}^{-1}$$

3. Calculate the energy emitted when electrons of 1.0 gm atom of Hydrogen undergo transition giving the spectral lines of lowest energy in visible region of its atomic spectra. Given that,  $R_H = 1.1 \times 10^7 \text{ m}^{-1}$ ,  $c = 3 \times 10^8 \text{ m/sec}$ ,  $h = 6.625 \times 10^{-34} \text{ J sec}$ .

Sol. Visible region of H-spectrum correspond to Balmer series  $n_1 = 2$ ,  $n_2 = 3$  (for minimum energy transition)

$$1/\lambda = R_H \left[ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \Rightarrow \frac{1}{\lambda} = R_H \left[ \frac{1}{2^2} - \frac{1}{3^2} \right] \Rightarrow \frac{1}{\lambda} = 1.1 \times 10^7 \left[ \frac{1}{4} - \frac{1}{9} \right]$$

$$[R_H = 109677 \text{ cm}^{-1} = 109677 \times 100 \text{ m}^{-1} \approx 1.1 \times 10^7 \text{ m}^{-1}]$$

$$\lambda = 6.55 \times 10^{-7} \text{ m}$$

$$E = \frac{hc}{\lambda} = \frac{6.625 \times 10^{-34} \times 3 \times 10^8}{6.55 \times 10^{-7}} = 3.03 \times 10^{-19} \text{ Joule}$$

$\therefore$  Energy released by 1 gm atom of H (1 mol)

$$= 3.03 \times 10^{-19} \times 6.023 \times 10^{23} = 18.25 \times 10^4 \text{ J} = 182.5 \text{ kJ}$$

---

**Exercise**


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Calculate ratio of wavelength of limiting line of Balmer and Paschen series for an atom .

**Ans.** 4/9

---

### 15.5 Failure of Bohr Model

- (i) Bohr theory was very successful in predicting and accounting the energies of line spectra of hydrogen i.e. one electron system. It could not explain the line spectra of atoms containing more than one electron.
- (ii) This theory could not explain the presence of multiple spectral lines.
- (iii) This theory could not explain the splitting of spectral lines in magnetic field (Zeeman effect) and in electric field (Stark effect). The intensity of these spectral lines was also not explained by the Bohr atomic model.
- (iv) This theory could not explain uncertainty principle.

## 16. PARTICLE AND WAVE NATURE OF ELECTRON

In 1924, de Broglie proposed that an electron, like light, behaves both as material particle and as a wave. This proposal gave a new theory, known as wave mechanical theory of matter. According to this theory, the electrons, protons and even atoms, when in motion, possess wave properties.

de Broglie derived an expression for calculating the wavelength of the wave associated with the electron. According to Planck's equation

$$E = h\nu = h \cdot \frac{c}{\lambda} \quad \text{.....(1)}$$

The energy of a photon on the basis of Einstein's mass-energy relationship is

$$E = mc^2 \quad \text{.....(2)}$$

where,  $c$  is the velocity of the electron.

From (1) and (2) equation

$$h \times \frac{c}{\lambda} = mc^2$$

$$\lambda = \frac{h}{mc} = \frac{h}{p} \quad \text{.....(3)}$$

Momentum of the moving electron is inversely proportional to its wavelength.

Let kinetic energy of the particle of mass ' $m$ ' is  $E$ .

$$E = \frac{1}{2} mv^2$$

$$2Em = m^2 v^2$$

$$\sqrt{2Em} = mv = p \text{ (momentum)}$$

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2Em}} \quad \text{.....(4)}$$

Let a charged particle, with charge  $q$  be accelerated with a potential of  $V$ ; then the kinetic energy may be given as :  $E = qV$

$$\frac{1}{2} mv^2 = qV$$


---

$$m^2v^2 = 2qVm$$

$$mv = \sqrt{2qVm}$$

and,  $\lambda = \frac{h}{\sqrt{2qVm}} \dots\dots\dots(5)$

**(A) de Broglie wavelength associated with charged particles**

For electron :  $\lambda = \frac{12.27}{\sqrt{V}} \text{ \AA}$

For proton :  $\lambda = \frac{0.286}{\sqrt{V}} \text{ \AA}$

For  $\alpha$  - particles :  $\lambda = \frac{0.101}{\sqrt{V}} \text{ \AA}$

where, V = accelerating potential of these particles

**(B) de Broglie wavelength associated with neutron**

For neutron :  $\lambda = \frac{h}{\sqrt{2Em}} = \frac{6.62 \times 10^{-34}}{\sqrt{2 \times 1.67 \times 10^{-27} \times E}} = \frac{0.286}{\sqrt{E(\text{eV})}} \text{ \AA}$

The wavelength decreases if the value of mass (m) increases i.e. de Broglie equation is applicable in the case of smaller particles like electron and has no significance for larger particles.

**Derivation of Angular Momentum from de Broglie Equation:**

According to Bohr's model, the electron revolves around the nucleus in circular orbits. According to de Broglie concept, the electron is not only a particle but also has a wave character. If the wave is completely in phase, the circumference of the orbit must be equal to an integral multiple of wave length ( $\lambda$ ).

$$2\pi r = n\lambda$$

where 'n' is an integer and 'r' is the radius of the orbit

But  $\lambda = h/mv$

$\therefore 2\pi r = nh/mv$

or  $mvr = nh/2\pi$

which is Bohr's postulate of angular momentum, where 'n' is the principal quantum number.

"Thus, the number of waves an electron makes in a particular Bohr orbit in one complete revolution is equal to the principal quantum number of the orbit".

**Illustration**

What is de Broglie wavelength for a hydrogen atom moving with a velocity of  $2000 \text{ ms}^{-1}$  ? (Atomic mass of hydrogen = 1.00797 a.m. u)

**Sol.** Mass of a hydrogen atom =  $\frac{1.0097}{6.02 \times 10^{23}} \text{ g} = 1.68 \times 10^{-24} \text{ g} = 1.68 \times 10^{-27} \text{ kg}$

$$\lambda = \frac{h}{mv} = \frac{6.62 \times 10^{-34}}{1.68 \times 10^{-27} \times 2000} = 1.97 \times 10^{-10} \text{ m}$$



**Exercise**

Determine the de Broglie's wavelength of electron emitted by a metal whose threshold frequency is  $2.25 \times 10^{14}$  Hz when exposed to visible radiation of wavelength 500 nm.

Ans. 9.84 Å

**17. HEISENBERG'S UNCERTAINTY PRINCIPLE**

- (a) While treating  $e^-$  as a wave it is not possible to ascertain simultaneously the exact position and velocity of the  $e^-$  more precisely at a given instant since the wave is extending throughout a region of space
- (b) As the photons of longer wavelengths are less energetic, hence they have less momentum and cannot be located exactly
- (c) In 1927, Werner Heisenberg presented a principle known as Heisenberg's uncertainty principle
- (d) According to this principle it is impossible to measure simultaneously the exact position and exact momentum of a body as small as an electron.
- (e) If uncertainty of measurement of position is  $\Delta x$  and uncertainty of measurement of momentum is  $\Delta p$  or  $m\Delta v$ , then according to Heisenberg

$$\Delta x \cdot \Delta p \geq \frac{h}{4\pi} \quad \text{or} \quad \Delta x \cdot m\Delta v \geq \frac{h}{4\pi}$$

where  $h$  is Planck's constant

- (f) For other conjugates of motion the equation for Heisenberg's uncertainty principle may be given as

$$\Delta E \cdot \Delta t \geq \frac{h}{4\pi} \quad (\text{for energy and time})$$

- (g) Like de Broglie equation, this principle has significance only for microscopic particles.

**Illustration**

An electron having velocity  $2 \times 10^6$  m/s has uncertainty in kinetic energy is  $\frac{6.62}{\pi} \times 10^{-21}$  J, then calculate the uncertainty in position (in Angstrom, Å) of the electron. [Given :  $h = 6.62 \times 10^{-34}$  J-sec]

Sol.  $KE = \frac{1}{2}mv^2$      $v = 2 \times 10^6$  m/s

$$d(KE) = mv dv$$

$$dv = \frac{d(KE)}{mv} \quad \dots(1)$$

$$\text{But } \Delta x = \frac{h}{4\pi m \Delta v} \quad \dots(2)$$

$$\Delta x = \frac{h}{4\pi m \frac{d(KE)}{mv}} \quad ; \quad \Delta x = \frac{6.62 \times 10^{-34} \times 2 \times 10^6}{4\pi \times \frac{6.62}{\pi} \times 10^{-21}} = 500 \text{ Å}$$



---

**Exercise**


---

1. A measurement establishes position of a proton with an accuracy of  $\pm 10^{-10}$  m. Find the minimum uncertainty in proton's position 1 second later.

Sol.  $\Delta x = \pm 10^{-10}$  m

$\therefore$  According to Heisenberg's Uncertainty Principle

$$\Delta v = \frac{h}{4\pi m(\Delta x)} = \frac{6.62 \times 10^{-34}}{4 \times 3.14 \times 1.67 \times 10^{-27} \times 10^{-10}} = 0.3156 \times 10^3$$

$$\Delta v = \Delta x / \Delta t$$

$$\text{hence } \Delta x (\text{minimum uncertainty in position after one sec.}) = \Delta v \times \Delta t \\ = 0.3156 \times 10^3 \times 1 = 3.15 \times 10^2 \text{ m Ans.}$$


---

## WAVE MECHANICAL MODEL OF ATOM

The atomic model which is based on the particle and wave nature of the electron is known as wave mechanical model of the atom. This was developed by Erwin Schrodinger in 1926. This model describes the electron as a three-dimensional wave in the electronic field of positively charged nucleus. Schrodinger derived an equation which described wave motion of an electron. The differential equation is :

$$\frac{d^2\psi}{dx^2} + \frac{d^2\psi}{dy^2} + \frac{d^2\psi}{dz^2} + \frac{8\pi^2m}{h^2} (E - V) \psi = 0$$

Where x, y and z are cartesian coordinates of the electron; m = mass of the electron; E = total energy of the electron; V = potential energy of the electron; h = Planck's constant and  $\psi$  (psi) = wave function of the electron.

**Significance of  $\psi$  :** The wave function may be regarded as the amplitude function expressed in terms of coordinates x, y and z. The wave function may have positive or negative values depending upon the values of coordinates.

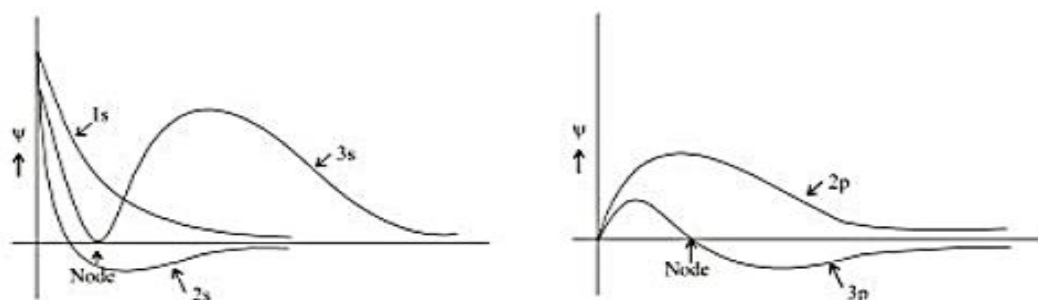
The main aim of Schrodinger equation is to give a solution for the probability approach. When the equation is solved, it is observed that for some regions of space, the value of  $\psi$  is positive and for other regions the value of  $\psi$  is negative. But the probability must be always positive and cannot be negative. It is, thus, proper to use  $\psi^2$  in favour of  $\psi$ .

**Significance of  $\psi^2$  :**  $\psi^2$  is a probability factor. It describes the probability of finding an electron within a small space. The space in which there is maximum probability of finding an electron is termed as orbital.

The important point of the solution of this equation is that it provides a set of number, called quantum numbers, which describe energies of the electrons in atoms, information about the shapes and orientations of the most probable distribution of electron around the nucleus.

Wave function  $\psi$  can be plotted against distance 'r' from nucleus as,

---



For hydrogen wave function, number of nodes can be calculated as,

- (i) Number of radial nodes =  $(n - l - 1)$
- (ii) Number of angular nodes =  $l$
- (iii) Total number of nodes =  $(n - 1)$

- Examples :**
- (i) For 1s – orbital  $n = 1, l = 0$ , it will have no radial or angular node
  - (ii) For 2s–orbital,  $n = 2, l = 0$ , it will have only one radial node
  - (iii) For 3s-orbital,  $n = 3, l = 0$ , it will have two radial nodes
  - (iv) For 2p-orbital,  $n = 2, l = 1$ , it will have no radial node but it has only one angular node
  - (v) For 3p-orbital,  $n = 3, l = 1$ , it will have one radial and one angular node

#### Solution of Schrodinger wave equation :

In spherical co-ordinates  $\psi(x, y, z)$  is represented by  $\psi(r, \theta, \phi)$  such that complete wave function can be given as

$$\psi(r, \theta, \phi) = \underbrace{R(r)}_{\text{Radial part}} \underbrace{\Theta(\theta)\Phi(\phi)}_{\text{Angular part}}$$

Dependence of the wave function on quantum number can be given as,

$$\Psi_{nlm}(r, \theta, \phi) = R_{nl}(r) \Theta_{lm}(\theta) \Phi_m(\phi)$$

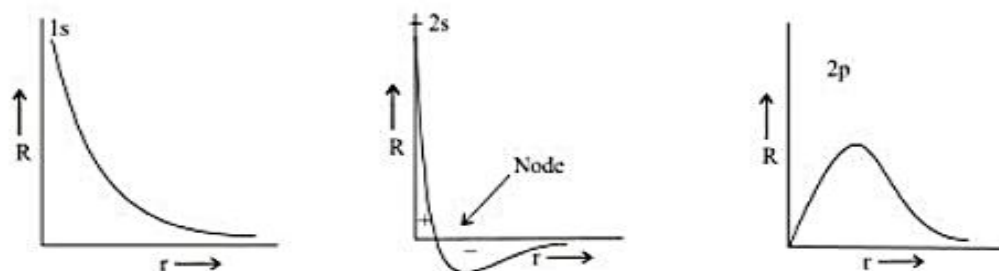
The function  $R$  depend only on  $r$ , therefore they describe the distribution of the electron as a function of  $r$  from the nucleus. These functions depend upon two quantum numbers,  $n$  and  $l$ . The two functions  $\Theta$  and  $\Phi$  taken together give the angular distribution of the electron.

The radial part the wave function for some orbitals may be given as,

	$n$	$l$	$R_{nl}$
1s	1	0	$2 \left( \frac{Z}{a_0} \right)^{3/2} e^{-Zr/a_0}$
2s	2	0	$\left( \frac{Z}{2a_0} \right)^{3/2} \left( 2 - \frac{Zr}{a_0} \right) e^{-Zr/2a_0}$
2p	2	1	$\frac{1}{\sqrt{3}} \left( \frac{Zr}{2a_0} \right)^{3/2} \left( \frac{Zr}{a_0} \right) e^{-Zr/2a_0}$

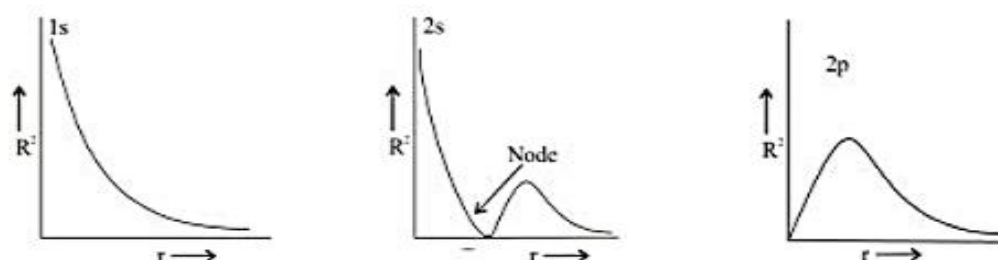
where,  $Z$  = atomic number,  $a_0$  = radius of first Bohr orbit of hydrogen.

### Plot of Radial Wave Function 'R':



At node, the value of 'R' changes from positive to negative.

### Plot of Radial Probability Density 'R<sup>2</sup>' :

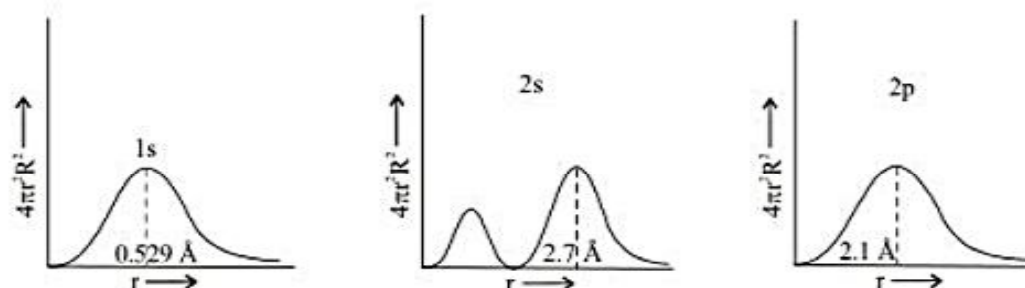


The plot of probability i.e.  $R^2$  or  $\Psi^2$  are more meaningful than the plots of function themselves. It can be seen that for both 1s and 2s orbitals, the probability has a maximum value at  $r=0$ , i.e. in the nucleus. In case of 2s orbital, one more maximum in the probability plot is observed.

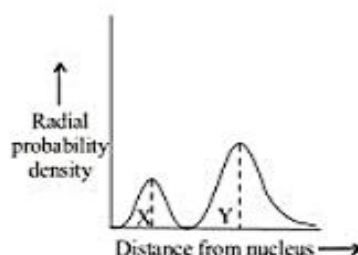
### Plot of Radial probability Function ( $4\pi r^2 R^2$ ) :

In order to visualize the electron cloud within a spherical shell is placed at radii ' $r$ ' and ' $r + dr$ ' from the nucleus. Thus radial probability function describes the total probability of finding the electron in a spherical shell of thickness ' $dr$ ' located at the distance  $r$  from the nucleus.

$$\text{R.P.E.} = (\text{Volume of spherical shell}) \times \text{Probability density} = (4\pi r^2 dr) \times R^2$$



In the plot of radial probability against ' $r$ ', number peaks, i.e. region of maximum probability =  $n - 1$ .

**Illustration**

If the above radial probability curve indicates '2s' orbital, the distance between the peak points X & Y is-

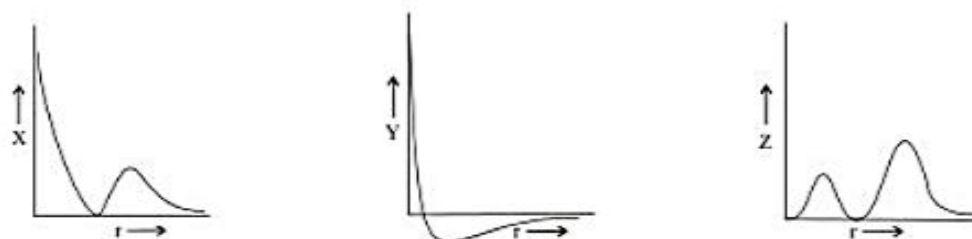
- (A) 2.07 Å      (B) 1.59 Å      (C) 0.53 Å      (D) 2.12 Å

**Ans.** (A)

**Sol.**  $X = 0.53 \text{ Å}$ ,  $Y = 2.6 \text{ Å}$   
 $Y - X = 2.6 - 0.53 = 2.07 \text{ Å}$

**Exercise**

Plots for 2s orbital are :



X, Y and Z are respectively

- (A)  $R$ ,  $R^2$  and  $4\pi r^2 R^2$     (B)  $R^2$ ,  $R$  and  $4\pi r^2 R^2$     (C)  $4\pi r^2 R^2$ ,  $R^2$  and  $R$     (D)  $R^2$ ,  $4\pi r^2 R^2$  and  $R$

**Ans.** (B)

**19. QUANTUM NUMBERS**

- The measurement scale by which the orbitals are distinguished, can be represented by sets of numbers called as quantum number.
- Quantum numbers are to specify and display to complete information about size, shape and orientation of the orbital. These are principle, azimuthal and magnetic quantum number, which follows directly from solution of schrodinger wave equation.
- Except to these quantum numbers, one additional quantum number designated as spin quantum number, which specify the spin of electron in an orbital.
- Each orbital in an atom is specified by a set of three quantum numbers and each electron is designated by a set of four quantum numbers.

**19.1 Principal quantum number (n) :**

- It was proposed by Bohr and denoted by 'n'.
- It determines the average distance between electron and nucleus, means it is denoted the size of atom.



- (c) It determine the energy of the electron in an orbit where electron is present.
- (d) The maximum number of an electron in an orbit represented by this quantum number as  $2n^2$ .
- (e) It gives the information of orbit K, L, M, N, ...
- (f) The value of energy increases with the increasing value of  $n$ .
- (g) It represents the major energy shell from which the electron belongs.

### 19.2 Azimuthal quantum number or angular quantum number ( $\ell$ ) -

- (a) It was proposed by Sommerfield and denoted by ' $\ell$ '.
- (b) It determines the number of subshells or sublevels to which the electron belongs.
- (c) It tells about the shape of subshells.
- (d) It also expresses the energies of subshells  $s < p < d < f$  (Increasing energy).
- (e) The value of  $\ell$  is integral values upto  $(n - 1)$ , starting from zero where ' $n$ ' is the number of principle shell.
- (f)

Value of $\ell$	0	1	2	3
Name of subshell	s	p	d	f
Shape of orbital	spherical	Dumbbell	Clover leaf (Except $d_{z^2}$ doughnut)	Complex

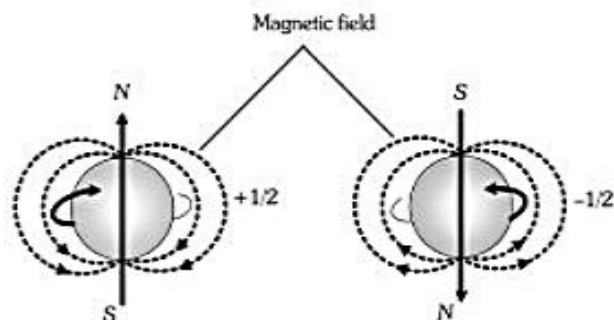
- (g) It represent the orbital angular momentum, which is equal to  $\frac{h}{2\pi} \sqrt{\ell(\ell+1)}$ .
- (h) The number of electrons in subshell =  $2(2\ell + 1)$ .
- (i) For a given value of ' $n$ ' the total value of ' $\ell$ ' is always equal to the value of ' $n$ '.

### 19.3 Magnetic quantum number ( $m$ ) :

- (a) It was proposed by Linde and denoted by ' $m$ '.
- (b) It gives the number of permitted orientation of subshells.
- (c) The value of  $m$  varies from  $-\ell$  to  $+\ell$  through zero.
- (d) It tells about the splitting of spectral lines in the magnetic field i.e. this quantum number proved the Zeeman effect.
- (e) For a given value of ' $n$ ' the total value of ' $m$ ' is equal to  $n^2$ .
- (f) For a given value of ' $\ell$ ' the total value of ' $m$ ' is equal to  $(2\ell + 1)$ .
- (g) *Degenerate orbitals* - Orbitals having the same energy are known as degenerate orbitals.  
e.g. for p subshell  $P_x$ ,  $P_y$  and  $P_z$  are degenerate orbital
- (h) The number of degenerate orbitals of s subshell = 0.

**19.4 Spin quantum number (s) :**

- (a) It was proposed by *Goldshmidt & Uhlenbeck* and denoted by the symbol of 's'.



- (b) The value of 's' is  $+\frac{1}{2}$  or  $-\frac{1}{2}$ , which is signified as the spin or rotation or direction of electron on its axis during the movement.
- (c) The spin may be clockwise or anticlockwise.
- (d) It represents the value of spin angular momentum is equal to  $\frac{h}{2\pi} \sqrt{s(s+1)}$ .
- (e) Maximum spin of an atom =  $\frac{1}{2} \times$  number of unpaired electron.

**Illustration**

1. The correct order of atomic orbitals in terms of energy between 8s and 8p orbital are  
 (A) 7d, 6f (B\*) 5g, 6f, 7d (C) 6d, 7f (D) 4h, 5g, 6f, 7d

Sol. (n+1): 8s  $\longrightarrow$   $8+0=8$   
 8p  $\longrightarrow$   $8+1=9$   
 5g  $\longrightarrow$   $5+4=9$   
 6f  $\longrightarrow$   $6+3=9$   
 7d  $\longrightarrow$   $7+2=9$   
 correct order  $\longrightarrow$  8s 5g 6f 7d 8p

2. Which of the following set of quantum number is valid/invalid. In case of valid set write the symbol of the orbital it represents [may have more than one answers] & in case it is invalid mention the reason.

	n	l	m
(i)	3	not known (but less than 3)	0

(ii)	-2	-1	+1
------	----	----	----

(iii)	4	2	-1
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- Sol. (i) Valid, 3s/3p<sub>x</sub>/3p<sub>y</sub>/3p<sub>z</sub>/3d <sub>$x^2-y^2$</sub> /3d <sub>$z^2$</sub> /3d<sub>xy</sub>/3d<sub>xz</sub>/3d<sub>yz</sub>  
 (ii) Invalid 'n' cannot be negative  
 (iii) Valid 4d <sub>$x^2-y^2$</sub> /4d <sub>$z^2$</sub> /4d<sub>xy</sub>/4d<sub>xz</sub>/4d<sub>yz</sub>

**Exercise**

How many electrons in a given atom can have the following quantum numbers –

- |                   |   |
|-------------------|---|
| (a) $n=4, \ell=1$ | (b) $n=2, \ell=1, m=-1, s=+\frac{1}{2}$ |
| (c) $n=3$         | (d) $n=4, \ell=2, m=0$                  |

Ans. (a) 6 (b) 1 (c) 18 (d) 2

## 20. SHAPE AND SIZE OF ORBITALS

An orbital is the region of space around the nucleus within which the probability of finding an electron of given energy is maximum (90-95%). The shape of this region (electron cloud) gives the shape of the orbital. It is basically determined by the azimuthal quantum number  $l$ , while the orientation of orbital depends on the magnetic quantum number ( $m$ ).

- 20.1 s-orbital ( $l = 0$ ):** These orbitals are spherical and symmetrical about the nucleus. The probability of finding the electron is maximum near the nucleus and keeps on decreasing as the distance from the nucleus increases. There is vacant space between two successive s-orbitals known as radial node. But there is no radial node for 1s orbital since it is starting from the nucleus.

The size of the orbital depends upon the value of principal quantum number ( $n$ ). Greater the value of  $n$ , larger is the size of the orbital. Therefore,

2s-orbital is larger than 1s orbital but both of them are non-directional and spherically symmetrical in shape.

- 20.2 p-orbital ( $l = 1$ ):** The probability of finding the p-electron is maximum in two lobes on the opposite sides of the nucleus. This gives rise to a dumb-bell shape for the p-orbital. For p-orbital  $l = 1$ . Hence,  $m = -1, 0, +1$ . Thus, p-orbital have three different orientations. These are designated as  $p_x$ ,  $p_y$  &  $p_z$  depending upon whether the density of electron is maximum along the x y and z axis respectively. As they are not spherically symmetrical, they have directional character. The two lobes of p-orbitals are separated by a nodal plane, where the probability of finding electron is zero.

The three p-orbitals belonging to a particular energy shell have equal energies and are called degenerate orbitals.

- 20.3 d-orbital ( $l = 2$ ):**

For d-orbitals,  $l = 2$ . Hence  $m = -2, -1, 0, +1, +2$ . Thus there are 5d orbitals. They have relatively complex geometry. Out of the five orbitals, the three ( $d_{xy}$ ,  $d_{yz}$ ,  $d_{zx}$ ) project in between the axis and the other two  $d_{x^2}$  and  $d_{x^2-y^2}$  lie along the axis.

- 20.4 Spherical nodes :** The spherical surface where probability of finding the electron is zero, is called spherical nodes.

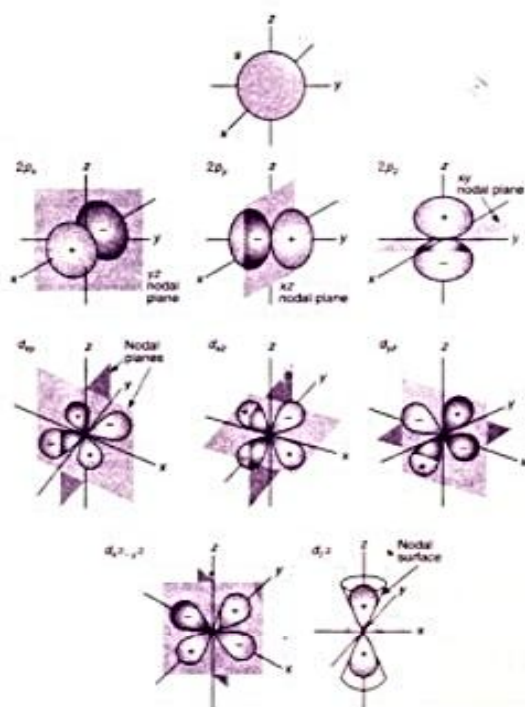
No. of spherical nodes in any orbital =  $n - l - 1$

- 20.5 Nodal Plane :** This is a plane passing through the nucleus where the probability of finding the electron is zero.

Number of nodal plane in a orbital =  $l$

Orbital	Nodal plane
$p_x$	yz
$p_y$	xz
$p_z$	xy
$d_{xy}$	yz, zx
$d_{yz}$	xy, xz
$d_{zx}$	xy, yz





## 21. ELECTRONIC CONFIGURATION

The distribution of electrons in different orbitals of atom is known as electronic configuration of the atoms.

Filling up of orbitals in the ground state of atom is governed by the following rules:

### 21.1 Aufbau principle

- (i) Auf bau is a German word, meaning 'building up'.
- (ii) According to this principle, "In the ground state, the atomic orbitals are filled in order of increasing energies i.e. in the ground state the electrons first occupy the lowest energy orbitals available".
- (iii) In fact the energy of an orbital is determined by the quantum number  $n$  and  $l$  with the help of  $(n+l)$  rule or Bohr Bury rule. According to this rule
  - (a) Lower the value of  $n + l$ , lower is the energy of the orbital and such an orbital will be filled up first.
  - (b) When two orbitals have same value of  $(n + l)$  the orbital having lower value of " $n$ " has lower energy and such an orbital will be filled up first.

Thus, order of filling up of orbitals is as follows:

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d$$

However, in one electron system, orbital of same principal quantum number have same energy, which is independent of  $(l)$ . In this system  $l$  only determines the shape of the orbital. Energy of orbitals are

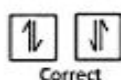
$$1s < 2s = 2p < 3s = 3p = 3d < 4s = 4p = 4d = 4f$$

### 21.2 Pauli's exclusion principle

- (i) According to this principle, "No two electrons in an atom can have same set of all the four quantum numbers  $n$ ,  $l$ ,  $m$  and  $s$  .



- (ii) In an atom any two electrons may have three quantum numbers identical but fourth quantum number must be different.
- (iii) Since this principle excludes certain possible combinations of quantum numbers for any two electrons in an atom, it was given the name exclusion principle. Its results are as follows :
- One orbital cannot have more than two electrons.
  - The maximum capacity of a main energy shell is equal to  $2n^2$  electrons.
  - The maximum capacity of a subshell is equal to  $2(2l + 1)$  electrons.
  - Number of sub-shells in a main energy shell is equal to the value of  $n$ .
  - Number of orbitals in a main energy shell is equal to  $n^2$ .
- (iv) According to this principle an orbital can accommodate at the most two electrons with spins opposite to each other. It means that an orbital can have 0, 1, or 2 electron.
- (v) If an orbital has two electrons they must be of opposite spin.



### 21.3 Hund's Rule of maximum multiplicity

- This rule provides the basis for filling up of degenerate orbitals of the same sub-shell.
- According to this rule "Electron filling will not take place in orbitals of same energy until all the available orbitals of a given subshell contain one electron each with parallel spin".
- This implies that electron pairing begins with fourth, sixth and eighth electron in p, d and f orbitals of the same subshell respectively.
- The reason behind this rule is related to repulsion between identical charged electron present in the same orbital.
- They can minimise the repulsive force between themselves by occupying different orbitals.
- Moreover, according to this principle, the electron entering the different orbitals of subshell have parallel spins. This keep them farther apart and lowers the energy through electron exchange.
- The term maximum multiplicity means that the total spin of unpaired is maximum in case of correct filling of orbitals as per this rule.

$$\text{Spin multiplicity} = (\text{no. of unpaired electron} + 1)$$

### Electronic configuration of some elements

S.No.	Elements	Symbol	Atomic No.	Electronic configuration
(1)	Hydrogen	H	1	$1s^1$
(2)	Nitrogen	N	7	$1s^2 2s^2 2p^3$ or $[\text{He}] 2s^2 2p^3$
(3)	Sulphur	S	16	$1s^2 2s^2 2p^6 3s^2 3p^4$ or $[\text{Ne}] 3s^2 3p^4$
(4)	Manganse	Mn	25	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$ or $[\text{Ar}] 3d^5 4s^2$

### Exceptional electronic configuration

S.No.	Elements	Symbol	Atomic No.	Electronic configuration
(1)	Chromium	Cr	24	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$ or $[\text{Ar}] 3d^5 4s^1$
(2)	Copper	Cu	29	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$ or $[\text{Ar}] 3d^{10} 4s^1$

Element	At.No.	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	6d	5f
H	1	1													
He	2	2													
Li	3	2	1												
Be	4	2	2												
B	5	2	2	1											
C	6	2	2	2											
N	7	2	2	3											
O	8	2	2	4											
F	9	2	2	5											
Ne	10	2	2	6											
Na	11	2	2	6	1										
Mg	12	2	2	6	2										
Al	13	2	2	6	2	1									
Si	14	2	2	6	2	2									
P	15	2	2	6	2	3									
S	16	2	2	6	2	4									
Cl	17	2	2	6	2	5									
Ar	18	2	2	6	2	6									
K	19	2	2	6	2	6		1							
Ca	20	2	2	6	2	6		2							
Sc	21	2	2	6	2	6	1	2							
Ti	22	2	2	6	2	6	2	2							
V	23	2	2	6	2	6	3	2							
*Cr	24	2	2	6	2	6	5	1							
Mn	25	2	2	6	2	6	5	2							
Fe	26	2	2	6	2	6	6	2							
Co	27	2	2	6	2	6	7	2							
Ni	28	2	2	6	2	6	8	2							
*Cu	29	2	2	6	2	6	10	1							
Zn	30	2	2	6	2	6	10	2							
Ga	31	2	2	6	2	6	10	2	1						
Ge	32	2	2	6	2	6	10	2	2						
As	33	2	2	6	2	6	10	2	3						
Se	34	2	2	6	2	6	10	2	4						
Br	35	2	2	6	2	6	10	2	5						
Kr	36	2	2	6	2	6	10	2	6						
Rb	37	2	2	6	2	6	10	2	6			1			
Sr	38	2	2	6	2	6	10	2	6			2			
Y	39	2	2	6	2	6	10	2	6	1		2			
Zr	40	2	2	6	2	6	10	2	6	2		2			
*Nb	41	2	2	6	2	6	10	2	6	4		1			
*Mo	42	2	2	6	2	6	10	2	6	5		1			
Tc	43	2	2	6	2	6	10	2	6	5		2			
*Ru	44	2	2	6	2	6	10	2	6	7		1			
*Rh	45	2	2	6	2	6	10	2	6	8		1			
*Pd	46	2	2	6	2	6	10	2	6	10					
*Ag	47	2	2	6	2	6	10	2	6	10		1			
Cd	48	2	2	6	2	6	10	2	6	10		2			
In	49	2	2	6	2	6	10	2	6	10		2	1		
Sn	50	2	2	6	2	6	10	2	6	10		2	2		

\* Exceptional electronic configuration

## 21.4 Extra stability of half filled and completely filled orbitals

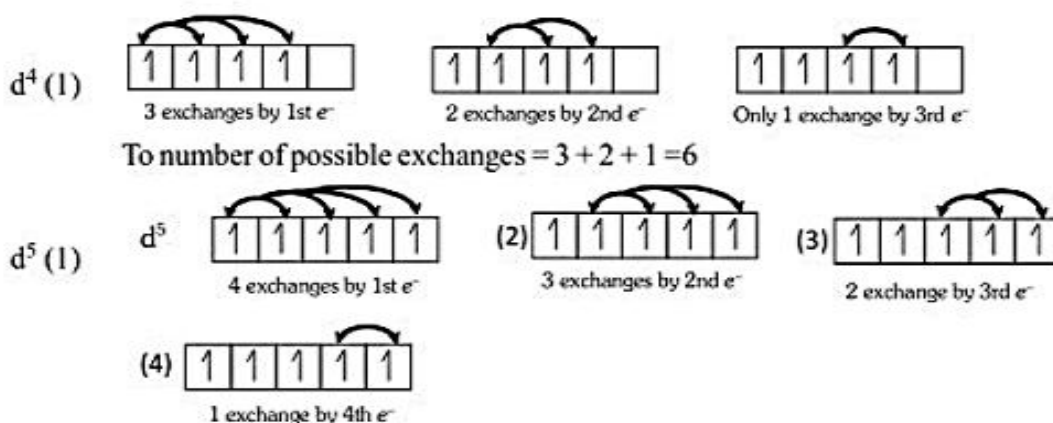
Half-filled and completely filled sub-shell have extra stability due to the following reasons :

### (i) Symmetry of orbitals

- It is a well known fact that symmetry leads to stability.
- Thus, if the shift of an electron from one orbital to another orbital differing slightly in energy results in the symmetrical electronic configuration. It becomes more stable.
- For example  $p^3, d^5, f^7$  configurations are more stable than their near ones.

### (ii) Exchange energy

- The electron in various subshells can exchange their positions, since electron in the same subshell have equal energies.
- The energy is released during the exchange process with in the same subshell.
- In case of half filled and completely filled orbitals, the exchange energy is maximum and is greater than the loss of energy due to the transfer of electron from a higher to a lower sublevel e.g. from 4s to 3d orbitals in case of Cu and Cr .
- The greater the number of possible exchanges between the electrons of parallel spins present in the degenerate orbitals, the higher would be the amount of energy released and more will be the stability.
- Let us count the number of exchange that are possible in and configuration among electrons with parallel spins.

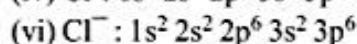
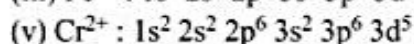
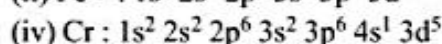
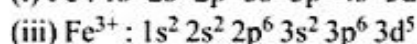
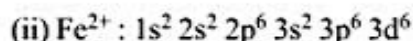
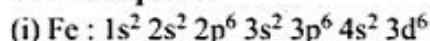


To number of possible exchanges = 4 + 3 + 2 + 1 = 10

## 21.5 Writing electronic configuration of ions

In ionization electron(s) are removed from outer-shell first (i.e. 4s) while, electrons are filled according to energy level.

**For example : -**





## SOLVED EXAMPLES

**Q.1** Electromagnetic radiations of wavelength 242 nm is just sufficient to ionise sodium atom. Calculate the ionisation energy of sodium in  $\text{kJ mol}^{-1}$ .

**Sol.** Energy associated with a photon of 242 nm  $= \frac{6.62 \times 10^{-34} \times 3.0 \times 10^8}{242 \times 10^{-9}} = 8.21 \times 10^{-19} \text{ joule}$

$\therefore$  1 atom of Na for ionisation requires  $= 8.21 \times 10^{-19} \text{ J}$

$\therefore 6.023 \times 10^{23}$  atoms of Na for ionisation requires  $= 8.21 \times 10^{-19} \times 6.023 \times 10^{23}$   
 $= 49.45 \times 10^4 \text{ J} = 494.5 \text{ kJ mol}^{-1}$

**Q.2** What transition in the hydrogen spectrum would have the same wavelength as the Balmer transition  $n = 4$  to  $n = 2$  of  $\text{He}^+$  spectrum?

**Sol.** For  $\text{He}^+$ ,  $Z = 2$   $\frac{1}{\lambda} = R_H Z^2 \left[ \frac{1}{2^2} - \frac{1}{4^2} \right]$

For H,  $Z = 1$   $\frac{1}{\lambda} = R_H \left[ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$

Since  $\lambda$  is same

$$\therefore 4 \left[ \frac{1}{2^2} - \frac{1}{4^2} \right] = \left[ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

$$\therefore \left[ \frac{1}{1^2} - \frac{1}{2^2} \right] = \left[ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \quad \therefore n_1 = 1 \text{ and } n_2 = 2$$

**Q.3** Calculate the longest wavelength which can remove the electron from I<sup>st</sup> Bohr's orbit. Given  $E_1 = 13.6 \text{ eV}$ .

**Sol.** The photon capable of removing electron from I Bohr's orbit must possess energy

$$= 13.6 \text{ eV}$$

$$= 13.6 \times 1.602 \times 10^{-19} \text{ J} = 21.787 \times 10^{-19} \text{ J}$$

$$\therefore E = \frac{hc}{\lambda};$$

$$21.787 \times 10^{-19} = \frac{6.62 \times 10^{-34} \times 3.0 \times 10^8}{\lambda}$$

$$\therefore \lambda = 912.24 \times 10^{-10} \text{ m} = 912.24 \text{ \AA}$$

**Q.4** Show that the wavelength of a 150 g rubber ball moving with a velocity  $50 \text{ m sec}^{-1}$  is short enough to be observed -

**Sol.**  $\therefore \lambda = \frac{h}{mv}$

Given  $v = 50 \text{ m sec}^{-1}$

$$= 50 \times 10^2 \text{ cm sec}^{-1}; m = 150 \text{ g}$$

$$\therefore \lambda = \frac{6.62 \times 10^{-27}}{150 \times 50 \times 10^2} = 8.83 \times 10^{-33} \text{ cm}$$

The wavelength is much lesser than that of visible region and thus it will not be visible.



**Q.5** An element undergoes a reaction as shown –

$X + 2e^- \longrightarrow X^{2-}$ , energy released = 30.87 eV/atom. If the energy released, is used to dissociate 8 gms of  $H_2$  molecules, equally into  $H^+$  and  $H^*$ , where  $H^*$  is an excited state of H atoms where the electron travels in orbit whose circumference equal to four times its de Broglie's wavelength.

(a) Calculate the excited state of H

(b) Determine the least amount of X that would be required.

Given : IE of H = 13.6 eV/atom, Bond energy of  $H_2$  = 4.526 eV/molecule.

**Sol.** (a)  $2\pi r = 4\lambda$

$$\therefore n = 4$$

(b)  $\therefore$  Total energy required

$$= 4 \times 4.526 \text{ eV} \times 6.023 \times 10^{23} + 4 \times 13.6 \times 6.023 \times 10^{23} + 4 \times 12.75 \text{ eV} \times 6.023 \times 10^{23}$$

$$= 4 \times 6.023 \times 10^{23} [30.876]$$

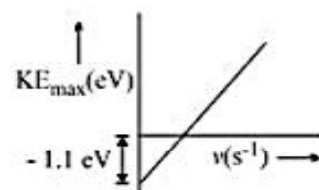
$$\therefore \text{moles of X required} = 4 \text{ moles}$$

**Q.6** Light of frequency  $7.5 \times 10^{14}$  Hz is incident on a metal surface. A curve between  $KE_{\max}$  v/s incident frequency is plotted as shown. Find

(a) The stopping potential

(b) Magnitude of the slope of curve given.

(c) Intercept on x-axis



**Sol.**  $KE_{\max} = h\nu - h\nu_0$  ....(1)

$h\nu_0 = 1.1 \text{ eV}$  (from the given curve)

Incident energy =  $h\nu$

$$= 6.62 \times 10^{-34} \times 7.5 \times 10^{14} \text{ J} \Rightarrow \frac{6.62 \times 10^{-20} \times 7.5}{1.6 \times 10^{-19}} \text{ eV} \Rightarrow 3.1 \text{ eV}$$

$$KE_{\max} = 3.1 - 1.1 = 2 \text{ eV}$$

We know that

(a) Stopping potential =  $KE_{\max} / e$   
= 2V

(b) Magnitude of slope of curve =  $h$

$$= \frac{6.62 \times 10^{-34} \text{ Js}}{1.6 \times 10^{-19}} \Rightarrow 4.14 \times 10^{-15}$$

(c) Intercept on x-axis = Threshold frequency

$$= \nu_0 = \frac{1.1 \text{ eV}}{h \text{ eV-s}} = \frac{1.1}{4.14 \times 10^{-15}} = 2.66 \times 10^{14} \text{ Hz} \quad \text{Ans.}$$

**Q.7** How many electrons in a given atom can have the following quantum numbers –

(a)  $n = 4, l = 1$

(b)  $n = 2, l = 1, m = -1, s = +\frac{1}{2}$

(c)  $n = 3$

(d)  $n = 4, l = 2, m = 0$

**Sol.** (a)  $l = 1$  refers to p - subshell which has three orbitals ( $p_x, p_y$  and  $p_z$ ) each having two electrons. Therefore, total number of electrons are 6.

(b)  $l = 1$  refers to p - subshell,  $m = -1$  refers to  $p_x$  or  $p_y$  orbital whereas,  $s = +\frac{1}{2}$  indicate for only 1 electron.

(c) Number of electrons for any energy level is given by

$$2n^2 \text{ i.e. } 2 \times 3^2 = 18 \text{ electrons}$$

(d)  $l = 2$  means d-subshell and  $m = 0$  refer to  $dz^2$  orbital

$\therefore$  Number of electrons are 2.

**Q.8** What designation will you assign to an orbital having following quantum number –

- (a)  $n = 3, \quad l = 1, \quad m = -1$
- (b)  $n = 5, \quad l = 0, \quad m = 0$
- (c)  $n = 2, \quad l = 1, \quad m = 0$

**Sol.** (a) Since  $l = 1$  corresponds to p-orbital and  $m = -1$  shows orientation either in x or y axis, thus this orbital refers to  $3p_x$  or  $3p_y$  or  $3p_z$   
 (b) 5s  
 (c)  $2p_z$  or  $2p_x$  or  $2p_y$

**Q.9** Which of the following set of quantum numbers are not permitted

- (a)  $n = 3, l = 2, m = -2, s = +1/2$
- (b)  $n = 3, l = 2, m = -1, s = 0$
- (c)  $n = 2, l = 2, m = +1, s = -1/2$

**Sol.** (a) This set of quantum number is permitted.  
 (b) This set of quantum number is not permitted as value of 's' cannot be zero.  
 (c) This set of quantum number is not permitted as the value of 'l' cannot be equal to 'n'.

**Q.10** (a) For any multielectron specie, compare the energies of following orbitals. **Justify** [External magnetic & electric fields are absent]

**Orbitals to be compared**  $3d_{xy}, 2s, 4p_x, 4p_y$

(b) Compare the "average distance" of the following orbitals from the nucleus. Also comment on their "Chances of closeness to the nucleus" if they have same average distance"

**Orbitals to be compared**  $1s, 2s, 3s, 3p_x, 3d_{xy}$

**Sol.** (a)  $2s < 3d_{xy} < 4p_x = 4p_y$   
 Justification compare  $(n + l)$  & if  $(n + l)$  same then 'n'  
 (b) Average distance (on the basis of n)  
 $1s < 2s < 3s = 3p_x = 3d_{xy}$   
 Closeness comparison  
 3s will be more close as compared to  $3p_x$  as compared to  $3d_{xy}$

**Q.11** Calculate energy of electron which is moving in the orbit that has its radius, sixteen times the radius of first Bohr orbit for H-atom.

**Sol.**  $r = r_0 n^2 \quad \Rightarrow n^2 = 16 \quad \Rightarrow n = 4$

$$E = \frac{-2.18 \times 10^{-18}}{n^2} = -1.36 \times 10^{-19} \text{ J/atom}$$

**Q.12** Wavelength of the Balmer  $H_\alpha$  line is 6565 Å. Calculate the wavelength of  $H_\beta$ , line of same hydrogen like atom.

**Sol.** For  $\alpha$ -line of Balmer Series

$$\frac{1}{\lambda_\alpha} = RZ^2 \left[ \frac{1}{2^2} - \frac{1}{3^2} \right]$$

For  $\beta$ -line of Balmer series

$$\frac{1}{\lambda_\beta} = RZ^2 \left[ \frac{1}{2^2} - \frac{1}{4^2} \right]$$

$$\frac{\lambda_{\beta}}{\lambda_{\alpha}} = \frac{\left[ \frac{1}{2^2} - \frac{1}{4^2} \right]}{\left[ \frac{1}{2^2} - \frac{1}{3^2} \right]}$$

$$\lambda_{\beta} = 4.863 \times 10^{-7} \text{ m}$$

- Q.13** The electron energy in hydrogen atom is given by  $E_n = \frac{-21.7 \times 10^{-12}}{n^2}$  ergs. Calculate the energy required to remove an  $e^-$  completely from  $n = 2$  orbit. What is the largest wavelength in cm of light that can be used to cause this transition.

**Sol.** For complete removal from  $n = 2$

$$\Delta E_n = +21.7 \times 10^{-12} \left[ \frac{1}{2^2} - \frac{1}{\infty^2} \right]$$

$$= 5.425 \times 10^{-12} \text{ erg}$$

$$\frac{hc}{\lambda} = \Delta E_n \quad \Rightarrow \quad \lambda = \frac{hc}{\Delta E_n} = 3.7 \times 10^{-5} \text{ cm}$$

- Q.14** Calculate the threshold frequency of metal if the binding energy is  $180.69 \text{ KJ mol}^{-1}$  of electron.

**Sol.**  $\Delta E \left( \text{in } \frac{\text{eV}}{\text{atom}} \right) = \frac{180.69 \times 10^3}{6.02 \times 10^{23} \times 1.6 \times 10^{-19}} = h\nu$

$$\nu = 4.5 \times 10^{14} \text{ S}^{-1}$$

- Q.15** U.V. light of wavelength  $800 \text{ \AA}$  &  $700 \text{ \AA}$  falls on hydrogen atoms in their ground state & liberates electrons with kinetic energy  $1.8 \text{ eV}$  and  $4 \text{ eV}$  respectively. Calculate planck's constant.

**Sol.**  $E_1 = \frac{hc}{\lambda_1} - \phi_0$        $E_2 = \frac{hc}{\lambda_2} - \phi_0$

$$E_1 - \frac{hc}{\lambda_1} = E_2 - \frac{hc}{\lambda_2} = \phi_0$$

$$hc \left( \frac{1}{\lambda_1} - \frac{1}{\lambda_2} \right) = E_1 - E_2$$

$$h = \frac{(E_2 - E_1) \lambda_1 \lambda_2}{(\lambda_1 - \lambda_2) c} = 6.57 \times 10^{-34} \text{ Js}$$

**Q.16** Through what potential difference must an electron pass to have a wavelength of 500 Å.

**Sol.**  $\lambda = \frac{h}{mv} = \frac{h}{\sqrt{2meV}}$

$$V = \left(\frac{h}{\lambda}\right)^2 \frac{1}{2me} = \frac{(6.63 \times 10^{-34})^2}{(5 \times 10^{-10})^2 \times 2 \times 9.01 \times 10^{-31} \times 1.6 \times 10^{-19}}$$

$$= 6.03 \times 10^{-4} \text{ V}$$

**Q.17** Calculate magnitude of orbital angular momentum of an  $e^-$  that occupies 1s, 2s, 2p, 3d, 3p.

[Ans. 0 ; 0 ;  $\sqrt{2} \frac{h}{2\pi}$  ;  $\sqrt{6} \frac{h}{2\pi}$  ;  $\sqrt{2} \frac{h}{2\pi}$  ]

**Sol.** Orbital angular momentum

$$= \frac{h}{2\pi} \sqrt{\ell(\ell+1)}$$

for 1s, 2s,  $\ell = 0$       O.A. M. = 0

for 2p,  $\ell = 1$       O.A.M. =  $\frac{h}{2\pi} \sqrt{2}$

for 3d,  $\ell = 2$       O.A.M. =  $\frac{h}{2\pi} \sqrt{6}$

for 3p,  $\ell = 1$ ,      O.A.M. =  $\frac{h}{2\pi} \sqrt{2}$



# ALKANE

## INTRODUCTION

### Alkanes

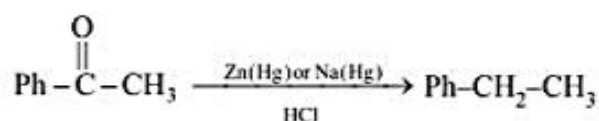
- (i) The alkanes or the paraffins are the saturated hydrocarbons. Many occur naturally, and the chief source of the alkanes is mineral oil or petroleum, which occurs in many parts of the world.
- (ii) These are also called as 'Paraffins' (Parum + Affinis i.e. less reactive).
- (iii) General formula is  $C_nH_{2n+2}$ .
- (iv) Hybridisation state of carbon is  $sp^3$ .
- (v) Geometry of carbon is tetrahedral.
- (vi) Bond angle is  $109^\circ 28'$ .

## PREPARATION OF ALKANE

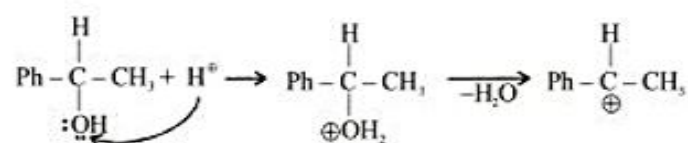
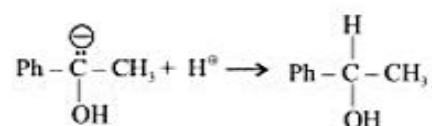
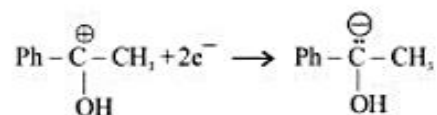
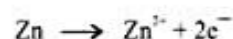
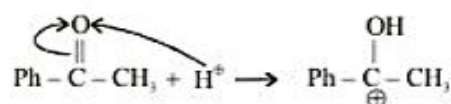
### From aldehydes and ketones :

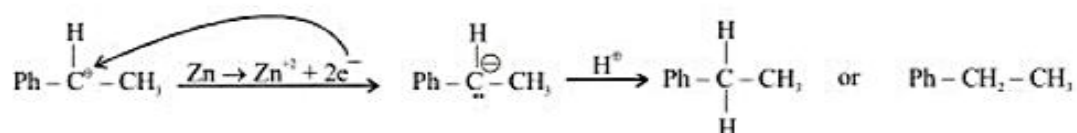
#### Clemmensen Reduction :

The Clemmensen reduction is most commonly used to convert acylbenzenes to alkylbenzenes, but it also works with other ketones and aldehydes that are not sensitive to acid. The carbonyl compound is heated with an excess of amalgamated zinc (zinc treated with mercury) and hydrochloric acid. The actual reduction occurs by a complex mechanism on the surface of the zinc.



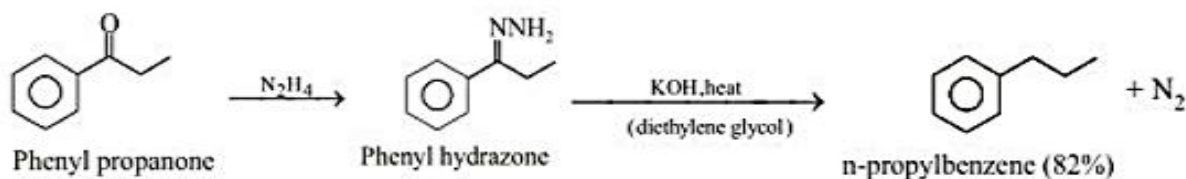
#### Mechanism



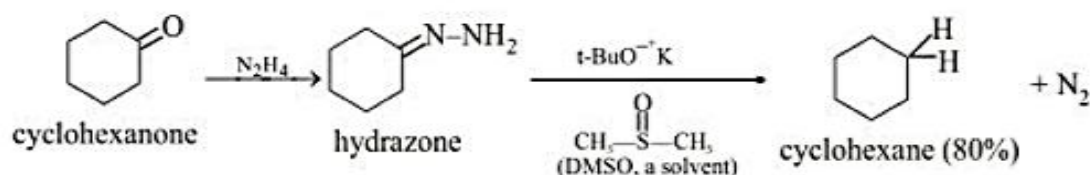
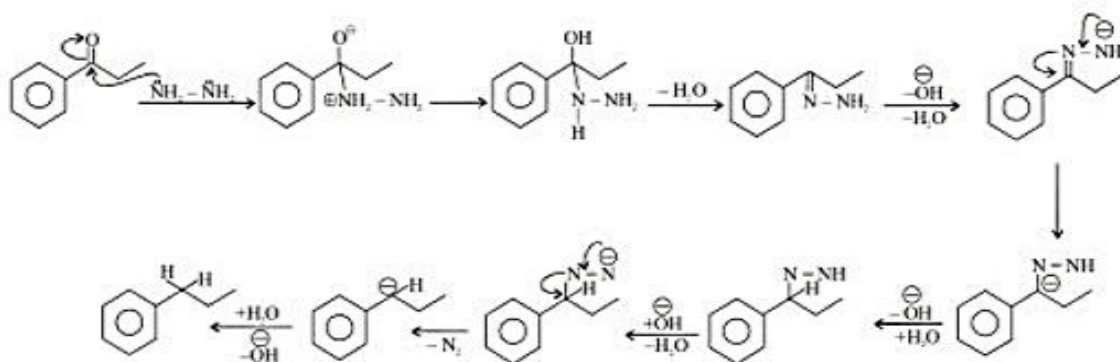


### Wolf-Kishner Reduction.

Compounds that cannot survive treatment with hot acid can be deoxygenated using the Wolf-Kishner reduction. The ketone or aldehyde is converted to its hydrazone, which is heated with a strong base such as KOH or potassium t-butoxide.



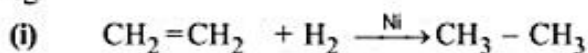
### Mechanism

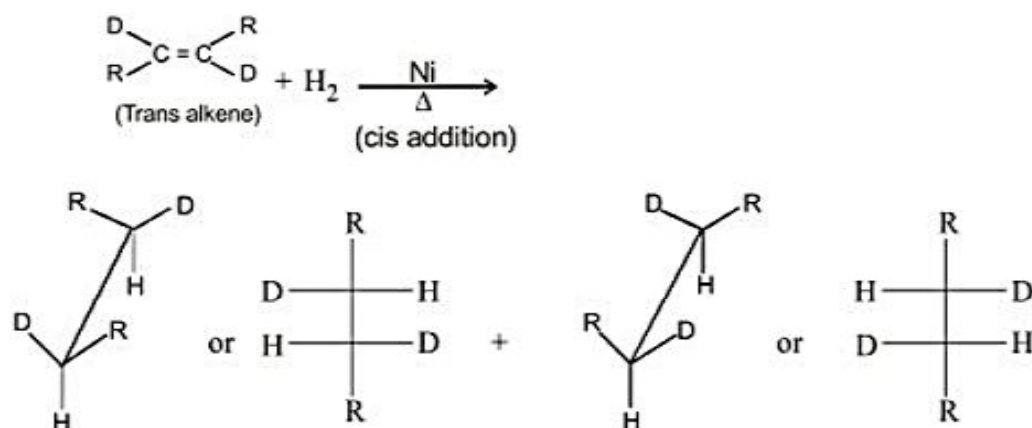
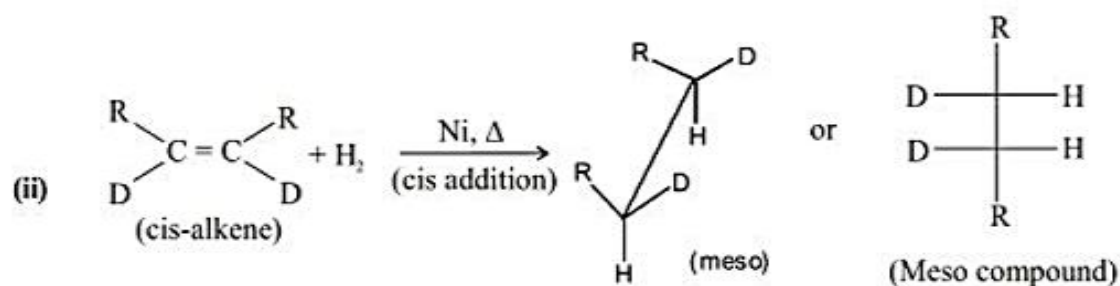


### From alkene :

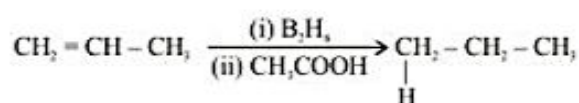
**By catalytic hydrogenation :** Addition of H<sub>2</sub> on alkene takes place in *cis manner* in the presence of Pt or Ni or Pd to give alkane.

eg.

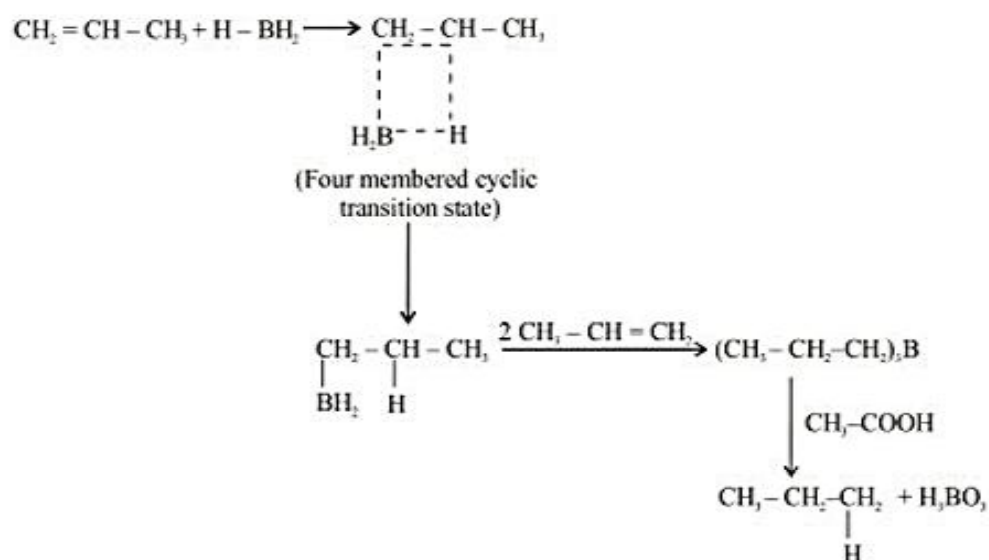




### By hydroboration reduction of alkene

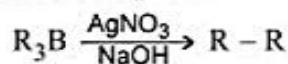


### Mechanism

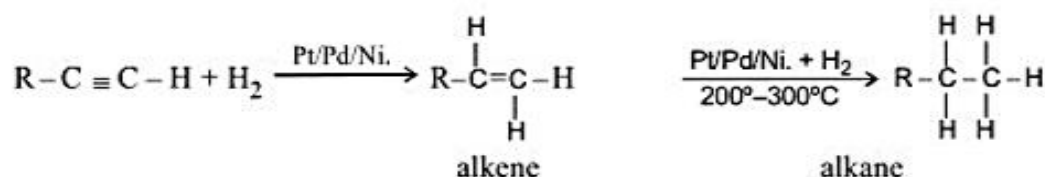


**NOTE :** Long-chain alkane may be possible by the coupling of alkyl boranes.

If  $(\text{AgNO}_3 + \text{NaOH})$  is used instead of  $\text{H}_2\text{O}/\text{H}^+$



From alkyne - by reduction :

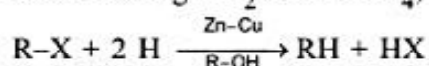


If Ni is used, it is called **Sabatier - Senderen's** reaction (catalytic hydrogenation).

From Alkyl halides :

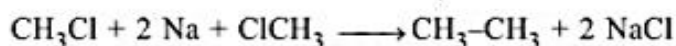
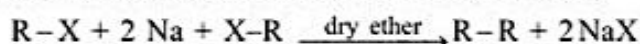
By reduction :

When alkyl halide is reduced with Zn-Cu couple + ROH or Na + EtOH/ Na- Hg + H<sub>2</sub>O or LiAlH<sub>4</sub>, then we get respective alkane.



Wurtz reaction :

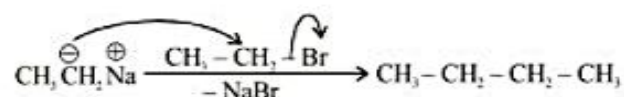
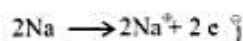
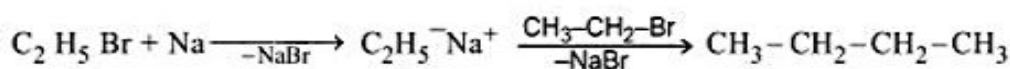
When alkyl halide reacts with Sodium in presence of dry ether then we get higher alkane. Mechanism of the reaction is based on ionic and free radical both.



**NOTE :** \* This reaction is not suitable for tertiary alkyl halides

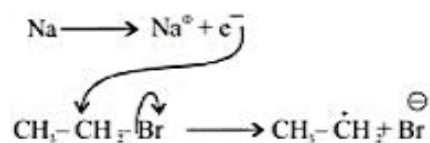
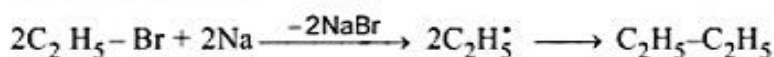
**Mechanism :** Two mechanism has been suggested for Wurt reaction.

Ionic mechanism

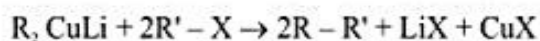
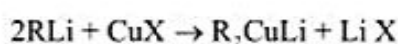
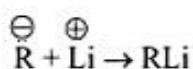
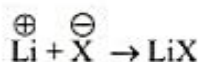
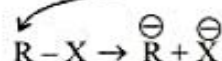
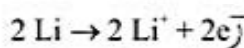
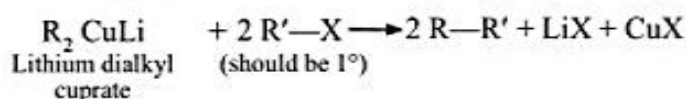
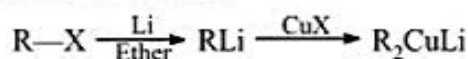




Free radical mechanism



**Corey-House Synthesis**



This method is better than Wurtz and can be used for preparing symmetrical as well as unsymmetrical alkanes (having an odd number of carbon atoms).

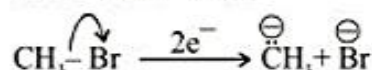
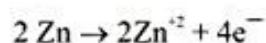
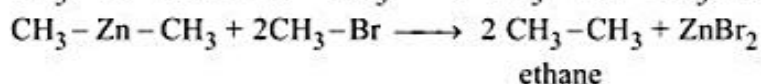
**Frankland's reaction :**

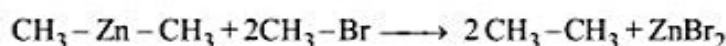
If alkyl halide is treated with Zn dust in closed tube then higher symmetrical alkanes will be formed.



This is known as Frankland's reaction, in this reaction first Frankland's reagent ( $\text{R}-\text{Zn}-\text{R}$ , dialkyl Zinc) is formed. Which then react with alkyl halide to give higher alkanes. [Where  $\text{R} = \text{CH}_3$ ]

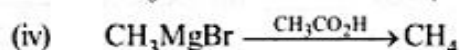
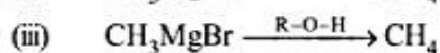
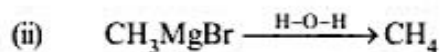
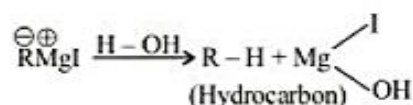
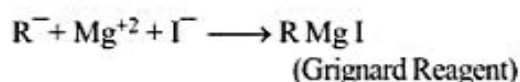
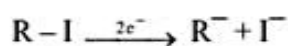
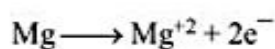
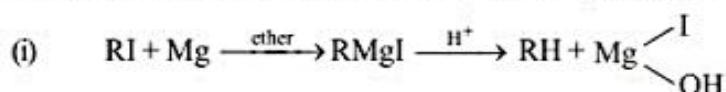
For Example:-





### Grignard reagents.

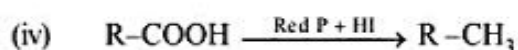
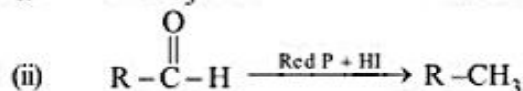
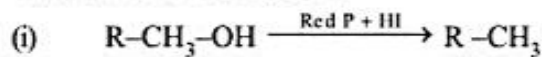
Alkyl halides in ether react with magnesium to form alkyl magnesium halides or Grignard reagents which, on treatment with water or dilute acid, are decomposed to alkanes.



Preparation by Wurtz reaction, Kolbe electrolysis Ulmann reaction, Fitting reaction, Wurtz-Fitting reaction already discussed in free radical reaction.

### From Red P + HI :

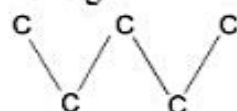
It is a powerful reducing agent which will convert, aldehyde, ketone, alcohol, carboxylic acid to alkanes with same number of carbon.



## PHYSICAL PROPERTIES

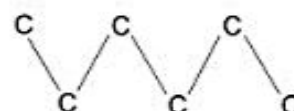
1. The first four alkanes (from methane to butane) are colourless and odourless gases. The next thirteen (from pentane to heptadecane) are colourless and odourless liquids. And, the rest of higher alkanes (having 18 carbon atoms or more) are colourless solids at ordinary temperature.
2. Alkanes being non-polar molecules, are soluble in non-polar solvents like benzene, ether, and chloroform. However, they are insoluble in polar solvents like water. Their solubility decreases with increase in their molecular weight.
3. Melting and boiling points are increases with molecular mass and decreases with No. branches. As far as melting point is concerned the alkane having even carbons has more M.P. than odd carbons, since the intermolecular forces in a crystal depend not only upon the size of the molecules but also upon how well they fit into a crystal lattice.

For e.g.



n- pentane

(both methyl group are directed on same side)

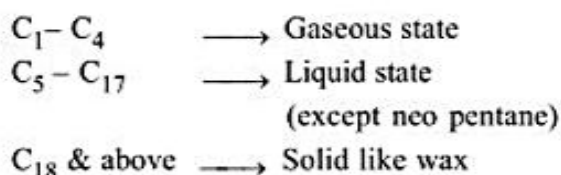


n- hexane

(both methyl group are adversely directed)

Melting point of alkane having odd number of 'c' < alkane with even number of carbom atom.

4. Boiling point decreases with the increment of branches.  
(n-Pentane is liquid but neo-Pentane is gas due to increase in branching, surface area decrease therefore intermolecular forces & Vander Waals forces of attraction decreases).
5. Physical state:  
Alkanes

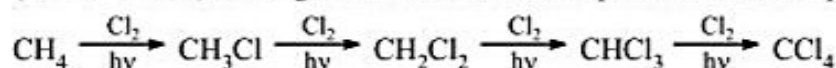


6. Alkanes are lighter than water, so it floats over water.

## CHEMICAL PROPERTIES

### 1. Halogenation

Alkanes react with bromine or chlorine in the presence of sunlight or UV light or in dark at high temperatures ( $250^\circ\text{C} - 400^\circ\text{C}$ ) forming a mixture of substituted products. For example,



The yield of monohalogenated product can be increased by using substrate (alkane) in excess.

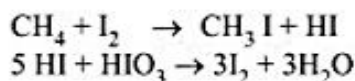
The reactivity of halogens follows the order:  $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$ .

Direct fluorination is explosive and can be achieved by the action of inorganic fluorides on bromo or iodo derivatives.

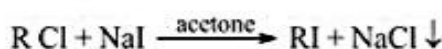


Bromination is slower than chlorination and is carried out at higher temperatures.

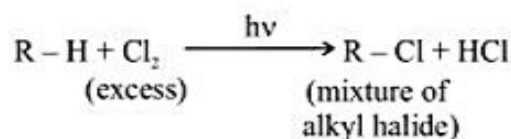
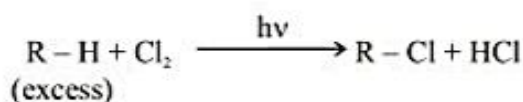
Iodination is reversible and can be carried out sufficiently in the presence of strong oxidising agents like iodic acid ( $\text{HIO}_3$ ) or nitric acid that destroys hydroiodic acid ( $\text{HI}$ ) and shifts the equilibrium towards the right.



Alkyl iodides can be prepared conveniently by **Finkelstein reaction** which involves treating chloro or bromoderivative with  $\text{NaI}$  in acetone or methanol solution.



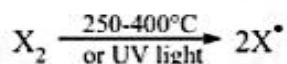
Alkyl chlorides or bromides cannot be prepared by this method of halide exchange because  $\text{NaCl}$  and  $\text{NaBr}$  are insoluble in acetone.



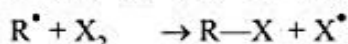
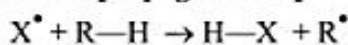
### Mechanism of Halogenation :

The mechanism involves the following steps:

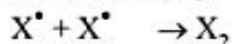
#### (i) Chain-initiation step



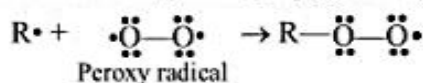
#### (ii) Chain-propagation step



#### (iii) Chain-termination step



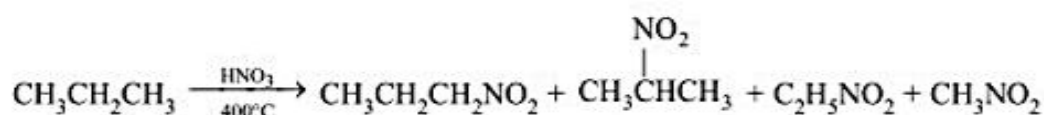
Radical inhibitors stop chain propagation by reacting with free radical intermediates.



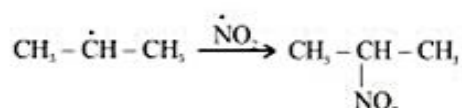
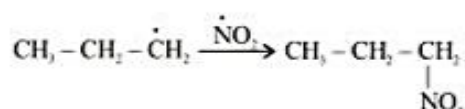
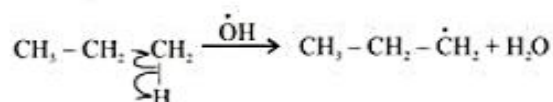
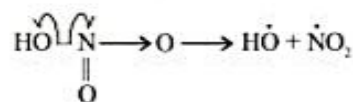
## 2. Nitration.

Under certain conditions, alkanes react with nitric acid, a hydrogen atom being replaced by a nitro-group,  $\text{NO}_2$ . This process is known as nitration. Nitration of the alkanes may be carried out in the vapour phase between  $150^\circ\text{C}$  and  $475^\circ\text{C}$ , whereupon a complex mixture of mononitroalkanes is obtained.





#### Mechanism



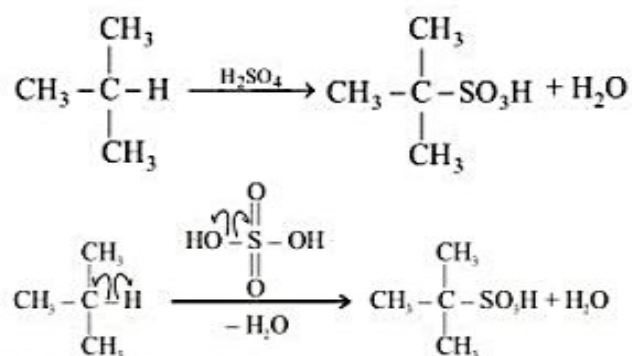
Similarly we deduce other products through some process.

### 3. Sulphonation.

Sulphonation is the process of replacing a hydrogen atom by a sulphonic acid group,  $\text{SO}_3\text{H}$ . Sulphonation of a normal alkane from hexane onwards may be carried out by treating the alkane with oleum (fuming sulphuric acid). It has been shown that in concentrated sulphuric acid, hydrocarbons containing a tertiary hydrogen atom undergo hydrogen exchange (Ingold et. al. 1936). The mechanism is believed to occur via a carbonium ion:



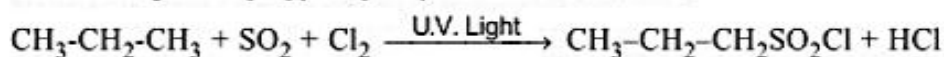
This reaction is of particular interest since optically active hydrocarbons have been racemised in sulphuric acid; e.g., Burwell et. al. (1948) have shown that optically active 3-methylheptane is racemised in sulphuric acid.



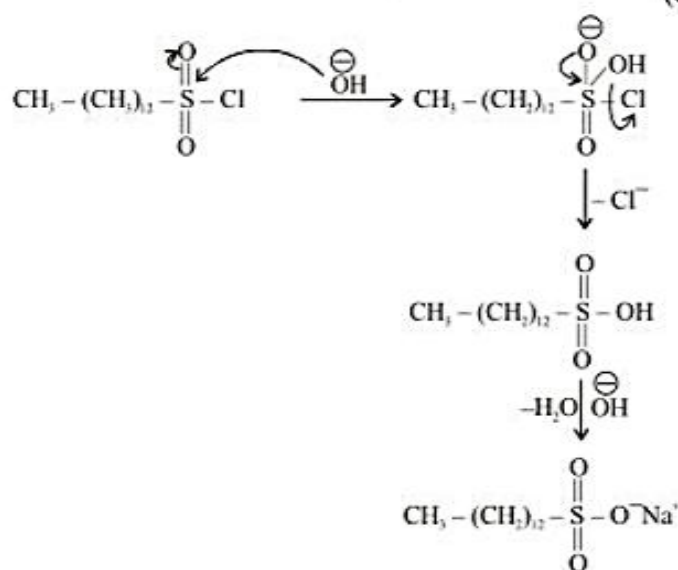
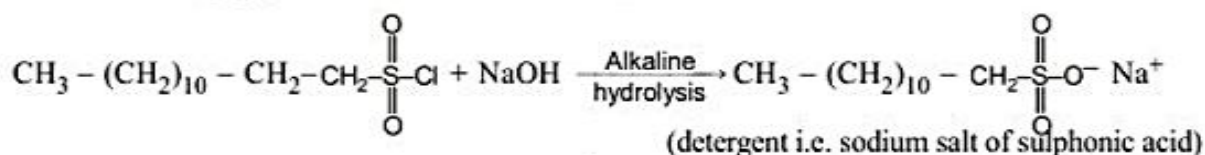
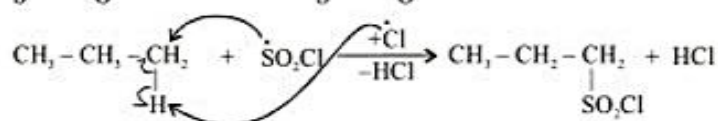
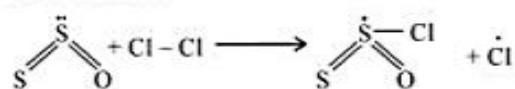
**Imp.** Rate of sulphonation  $3^\circ > 2^\circ > 1^\circ$ .

### 4 Chlorosulphonation/Reaction with $\text{SO}_2$ & $\text{Cl}_2$ :

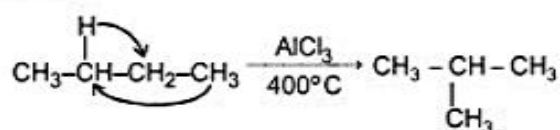
The reaction is also called as **Reed's reaction**. When propane reacts with  $\text{SO}_2$  and  $\text{Cl}_2$  in presence of ultraviolet light then propyl sulphonyl chlorides are formed.



This process is used in the commercial formation of detergents.

**Mechanism**

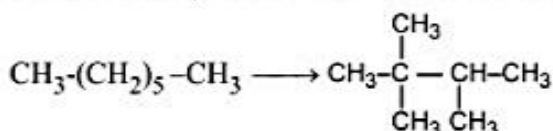
5. **Isomerization** : Lower alkanes are not isomerised but butane or higher number of alkanes if heated with aluminium chloride at high temperature then they convert into stable isomers by the rearrangement reaction. Isomerisation is also held by heating alkane with- ( $\text{AlX}_3 + \text{HX}$ ;  $\text{X} = \text{Cl}, \text{Br}, \text{I}$  or  $\text{Al}_2(\text{SO}_4)_3 + \text{H}_2\text{SO}_4$ ) at  $200^\circ\text{C}$ .



n - butane

iso butane

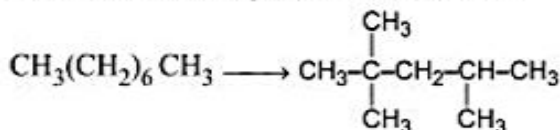
If we take n - heptane then it converts into most stable form Triptane (trivial name).



n - heptane

2, 2, 3- trimethyl butane

If we take n - octane, iso-octane is formed.



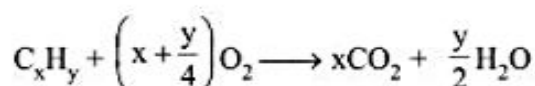
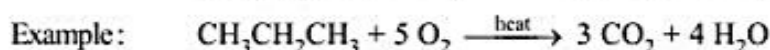
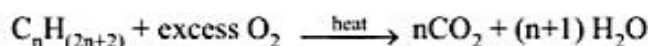
n - octane

iso-octane

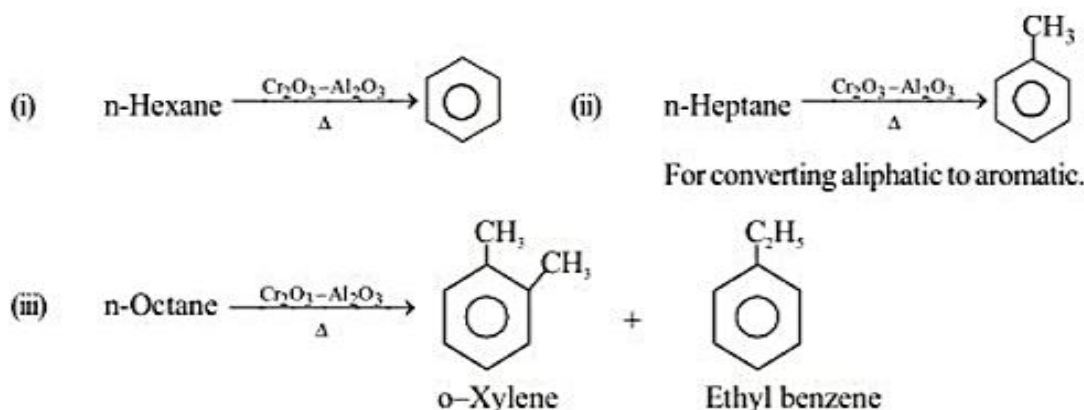
Reaction is used in Petroleum industries, with the help of this reaction, we can convert unbranched alkane to branched alkane (i.e. lower octane number alkane to higher octane number alkane) or bad fuel to good fuel.

#### 6. Combustion :

Combustion is a rapid oxidation that takes place at high temperatures, converting alkanes to carbon dioxide and water. Little control over the reaction is possible, except for moderating the temperature and controlling the fuel / air ratio to achieve efficient burning.



#### 7. Aromatization :



### MCQ

- Q.1 The Kolbe synthesis of alkane using a sodium salt of butanoic acid gives -  
 (A) n-hexane      (B) isobutane      (C) n-butane      (D) propane
- Q.2 Electrolysis of an aqueous solution of sodium butanoate gives main product -  
 (A) octane      (B) heptane      (C) hexane      (D) butane
- Q.3 In Wurtz reaction if we take  $CH_3Cl$  &  $C_2H_5Cl$  then product will be -  
 (A) Propane + Ethane      (B) Propane  
 (C) Propane + Ethane + Butane + Ethene +  $CH_4$       (D) Propane + Butane
- Q.4 Butane cannot be obtained by :  
 (A) Action of soda lime on sodium butanoate  
 (B) Clemmensen reduction (Zn amalgam in conc. HCl) of butanone  
 (C) Action of water on butyl magnesium iodide  
 (D) Sabatier Senderens hydrogenation of butene.

- Q.5** The reaction conditions leading to the best yields of  $C_2H_5Cl$  are –  
 (A)  $C_2H_6$  (Excess) +  $Cl_2 \xrightarrow{u.v. light}$  (B)  $C_2H_6 + Cl_2 \xrightarrow{dark\ room\ temp.}$   
 (C)  $C_2H_6 + Cl_2$  (Excess)  $\xrightarrow{u.v. light}$  (D)  $C_2H_6 + Cl_2 \xrightarrow{u.v. light}$
- Q.6**  $C_2H_6 + SO_2 + Cl_2 \xrightarrow{U.V. Light}$  product. In this reaction product will be -  
 (A)  $C_2H_4$  (B)  $CH_3CH_2Cl$  (C)  $CH_3CH_2SO_2Cl$  (D)  $C_2H_2$
- Q.7** Which of the following should be subjected to Wurtz reaction to obtain the best yield of n-hexane?  
 (A) Ethyl chloride and n-butyl chloride (B) Methyl bromide and n-propyl bromide  
 (C) n-Propyl bromide (D) Ethyl bromide and n-butyl bromide
- Q.8** 2-Methylbutane on reacting with bromine in the presence of sunlight gives mainly -  
 (A) 1-Bromo-3-methylbutane (B) 2-Bromo-3-methylbutane  
 (C) 2-Bromo-2-methylbutane (D) 1-Bromo-2-methylbutane
- Q.9** Which of the following alkyl bromides may be used for the synthesis of 2, 3-dimethylbutane by Wurtz reaction?  
 (A) n-Propyl bromide (B) Isopropyl bromide (C) Isobutyl bromide (D) s-Butyl bromide

#### ANSWER KEY

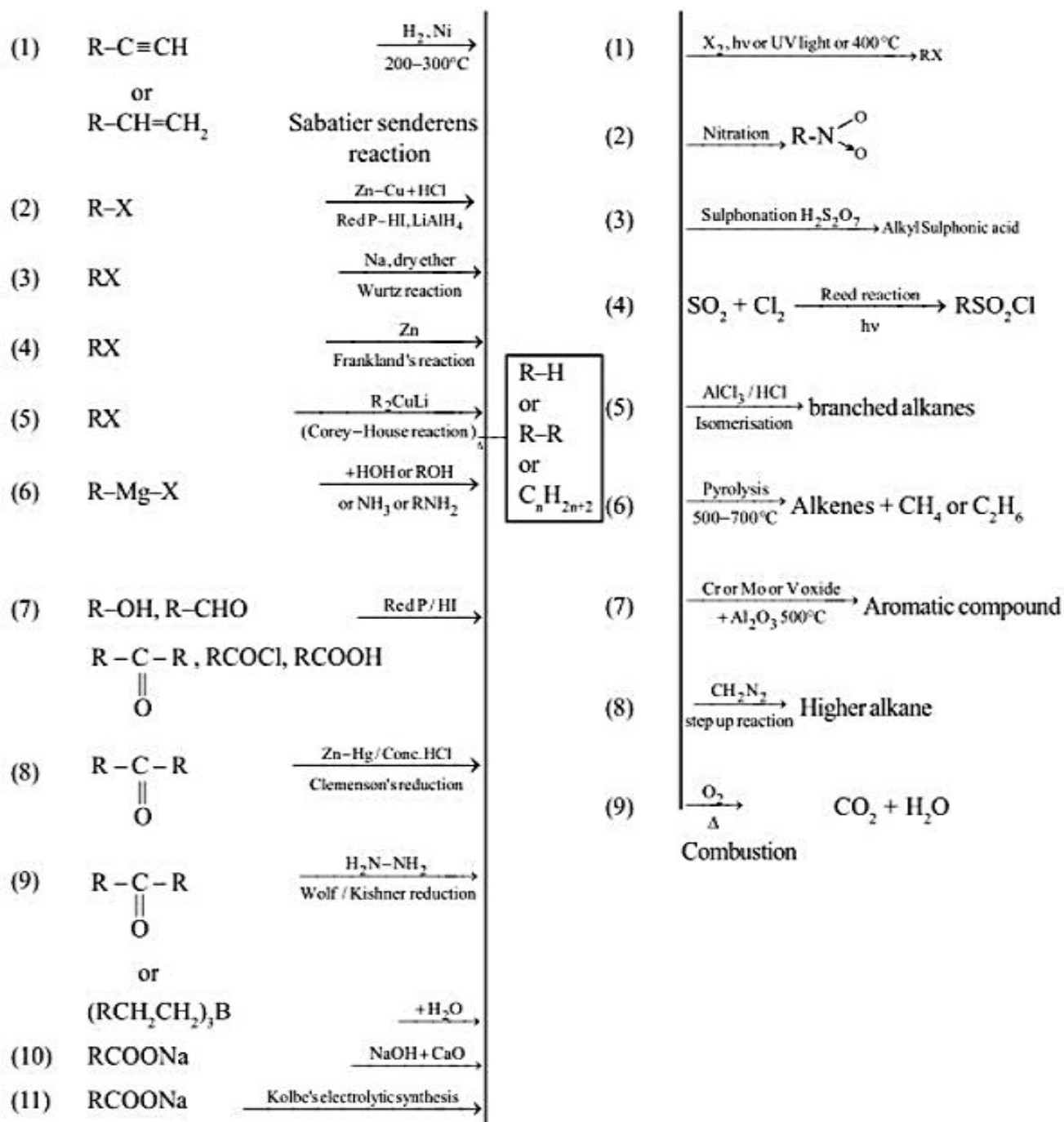
<b>Q.1</b>	A	<b>Q.2</b>	C	<b>Q.3</b>	C	<b>Q.4</b>	A
<b>Q.5</b>	A	<b>Q.6</b>	C	<b>Q.7</b>	C	<b>Q.8</b>	C
<b>Q.9</b>	B						



# REACTION CHART FOR ALKANES

GMP

GR



R-H  
or  
R-R  
or  
C<sub>n</sub>H<sub>2n+2</sub>

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## ALKENE

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### ALKENE

- (a) General formula :  $C_nH_{2n}$ .
- (b) Functional group : in alkenes is  $>C=C<$
- (c) The double bond is made up of one sigma and one pi bond.
- (d) The doubly bonded carbon atoms are  $sp^2$  hybridized.
- (e) Geometry of unsaturated 'C' carbon is trigonal planar.
- (f)  $C=C$  bond length is 1.34 Å.
- (g)  $C-H$  bond length is 1.10 Å.
- (h)  $C=C$  bond energy is 143.1 k cal mol<sup>-1</sup>.
- (i)  $C-H$  bond energy is 98.69 k cal mol<sup>-1</sup>.
- (j) Alkene shows chain, position, ring chain, optical & geometrical isomerism.

### METHODS OF PREPARATION OF ALKENES

#### Elimination reactions

Elimination reactions consist in removing the two groups (generally one being a proton and other is leaving group from one or two carbon atoms of a substrate to form an unsaturated linkage.

Elimination reactions are classified under two general categories.

#### Types of Elimination reactions

1.  $\alpha$ -elimination (1, 1)
2.  $\beta$ -elimination (1, 2)

1.  **$\alpha$ -elimination** : When the two atoms or groups are eliminated from the same carbon, the process is called  $\alpha$ -elimination.
2.  **$\beta$ -elimination** : When the two groups or atoms are removed from the two adjacent carbon atoms, the process is known as  $\beta$ -elimination.

#### Some important terms

- (1) **Substrate** : That molecule or ion which undergoes change is called substrate. Substrate may be alkyl halide, alcohol etc.
- (2) **Base** : It is negative ion or neutral molecule which abstract the proton from the substrate.
- (3) **Leaving Group** : It is an ion or molecule which leaves the substrate with a pair of electron. The tendency of leaving group is inversely proportional to basic strength. Leaving group ability of different halide ions follows the sequence  

$$I^- > Br^- > Cl^- > F^-$$

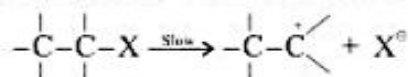
#### $\beta$ -Elimination can occur by three different mechanism

- (1) E-1 mechanism
  - (2) E-2 mechanism
  - (3) E1 cB mechanism
-

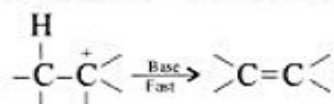
## E-1 MECHANISM

- (a) It is called unimolecular elimination reaction.  
 (b) It takes place in two steps.

**I<sup>st</sup> Step :** Departure of leaving group from a molecule to form carbocation.



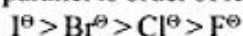
**II<sup>nd</sup> Step :** Carbocation formed above loses a proton to the base and forms the alkene.



- (c) 1<sup>st</sup> step of E-1 mechanism is the rate determining step (R.D.S.)  
 (d) Since in R.D.S. only substrate undergoes covalency change.  
 i.e. it follows first order kinetics with respect to substrate  
 $\text{Rate} = K [\text{substrate}]$   
 (e) Since in R.D.S. carbocation is formed as an intermediate so the reactivity order of different substrate follows the stability of order of carbocation formed.  
 Allylic > Tertiary > Secondary > Primary  
 (f) Loss of leaving group is the part of R.D.S. therefore the order of reactivity of alkyl halide in elimination reaction is



Above order is parallel to order of leaving group ability



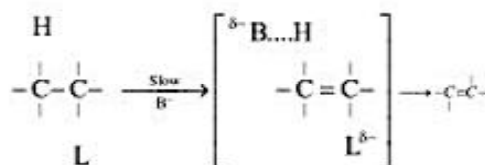
- (g) E-1 mechanism does not show isotopic effect as the loss of hydrogen is not the part of R.D.S.

$$\frac{K_H}{K_D} = 1$$

- (h) Since the ionization take place in step I. Therefore polar solvent favors the E-1 mechanism.  
 (i) E-1 mechanism involves carbocation as an intermediate so rearrangement of carbocation can take place if possible. More stable carbocation forms the major product in the reaction.

## E-2 MECHANISM

- (a) It is known as bimolecular elimination mechanism.  
 (b) It take place in single step.  
 (c) It involves the formation of transition state



Transition State

- (d) Formation of transition state is the rate determining step.  
 (e) Rate of reaction depends on the concentration of substrate as well as of base i.e. it follows the second-order kinetics.

$$\text{Rate} = [\text{Substrate}] [\text{Base}]$$

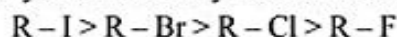


- (f) E-2 mechanism shows the isotopic effect as the loss of hydrogen is a part of R.D.S.

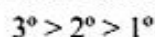
$$\frac{K_H}{K_D} = \frac{7}{1}$$

- (g) E-2 mechanism shows the halogen effect as loss of leaving group is a part of R.D.S.

∴ Reactivity of different alkyl halides follows the sequence



Reactivity order of different substrate follows

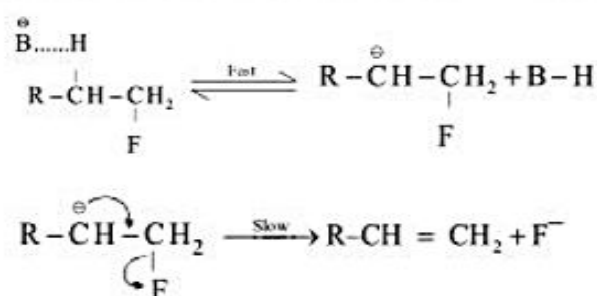


- (h) The rate of reaction increases with increasing strength and concentration of the base.  
 (i) Non-polar solvent favors the E-2 mechanism.  
 (j) Since E-2 mechanism involves the transition state rearrangement is not possible.

### E1 cB MECHANISM

- (a) In this mechanism, the reaction take place in two steps.

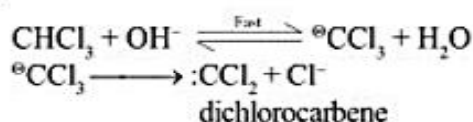
- (i) The first step involves rapid removal of a proton from the  $\alpha$ -carbon (carbon adjacent to the carbon bearing halogen atom) forming a carbanion.  
 (ii) The carbanion formed then loses the halides ion in the second rate determining step.



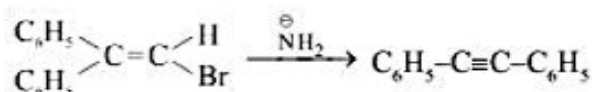
- (b) The overall rate of the reaction is limited to slower second step & hence the rate of reaction depends only on the concentration of carbanion.  
 (c) Since carbanion is the conjugate base of the alkyl halide and rate of reaction depends on concentration of carbanion hence the mechanism is designated as E1cB mechanism.

### Mechanism of $\alpha$ -Elimination

$\alpha$ -elimination does not occur frequently and completes in two stages, the second of which is rate determining for eq.

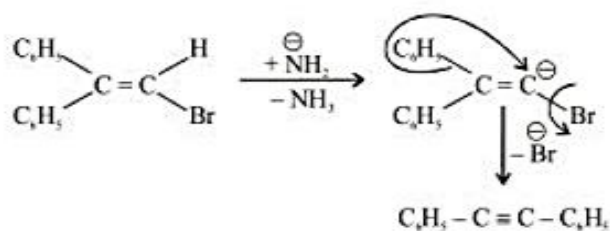


Another example of  $\alpha$ -elimination reaction is formation of diphenylacetylene from 2, 2-diphenyl vinyl bromide and sodamide.

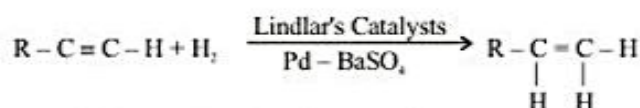




## Mechanism

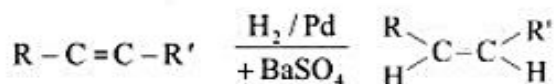


## From Alkynes

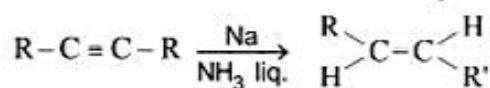


poison of catalyst such as  $\text{BaSO}_4$ ,  $\text{CaCO}_3$  are used to stop the reaction after the formation of alkene, otherwise alkanes are formed.

- (i) The reaction takes place at the surface of Pd, that is why it is *cis addition* and the product is cis form eg.

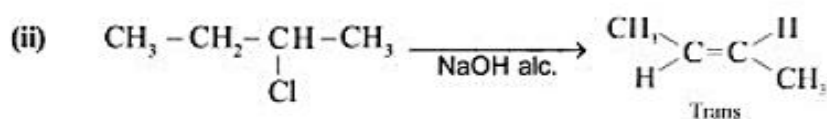
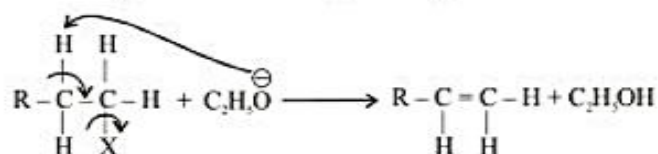
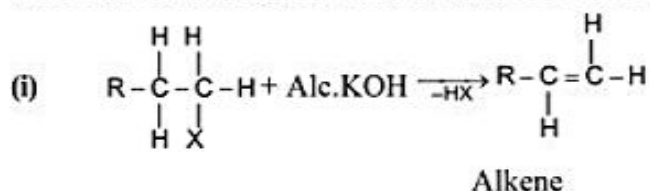


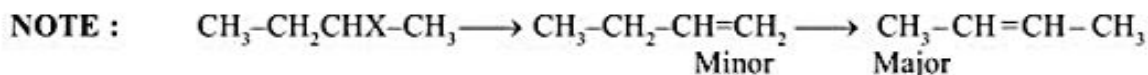
- (ii) Alkyne can be reduced to trans alkene by using  $\text{Na} + \text{NH}_3$ , or  $\text{LiAlH}_4$



## From mono halides

When mono halide react with alcoholic KOH or NaOH then respective alkenes are formed

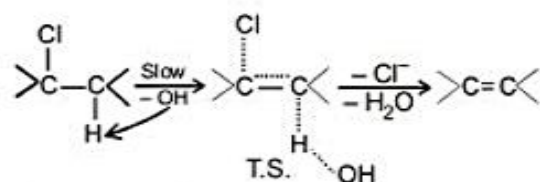




$\text{CH}_3\text{---CH=CH---CH}_3$  (Trans) is the major product because it is more stable as having six 'α' Hydrogen in the comparison to  $\text{CH}_3\text{---CH}_2\text{---CH=CH}_2$  having only two 'α' hydrogen. This is in accordance with the **saytzeff rule**.

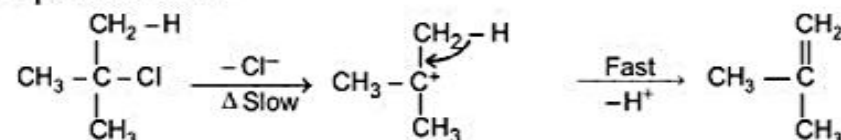
**Mechanism :**  $\text{E}_2$  and  $\text{E}_1$  are possible.

**$\text{E}_2$  Mechanism :**



As molecularity of slowest step is two i.e.  $\text{E}_2$  mechanism.

**$\text{E}_1$  Mechanism :-**

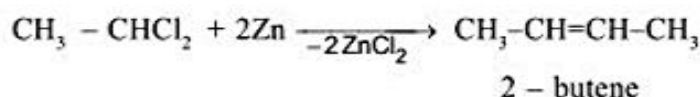
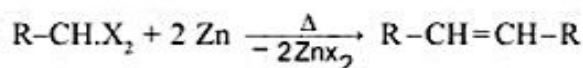


As molecularity of slowest step is **one**. That is why it is termed as  $\text{E}_1$ .

**Remember :** Possibility of  $\text{E}_1$  increases with increasing stability of carbo cation . Similarly possibility of  $\text{E}_2$  increases with decreasing stability of expected carbocation.

**From Dihalides**

**From gem dihalides :** When gem dihalide is heated with Na in ether then higher alkenes are formed.

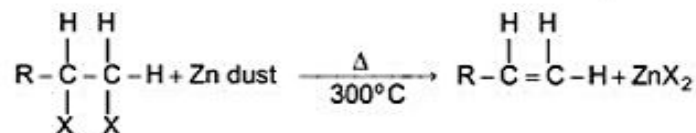


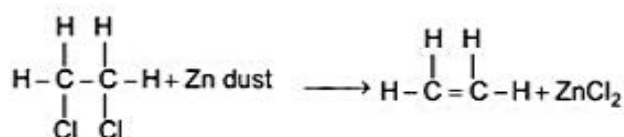
**Conclusion** – If we take two different types of gemdihalides then we obtain three different types of alkenes.

**Note :** The above reaction is used in the formation of symmetrical alkenes only, because if we take two different types of halides then mixture of alkenes is obtained so the yield of an individual alkene is reduced and it is improper to separate each alkene from the mixture because the difference of boiling points in alkenes is very less.

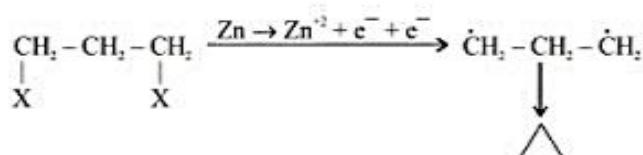
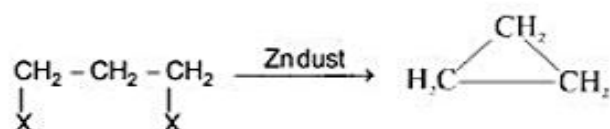
**From vicinal dihalides :**

When vicinal dihalides are heated with Zn dust, alkene of same no. of carbon is obtained.



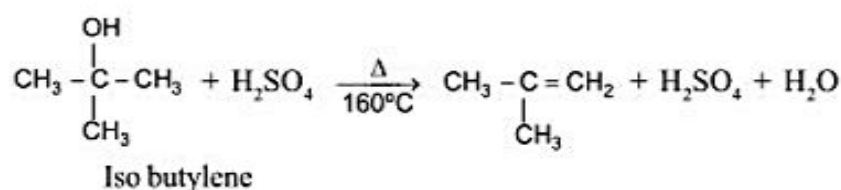
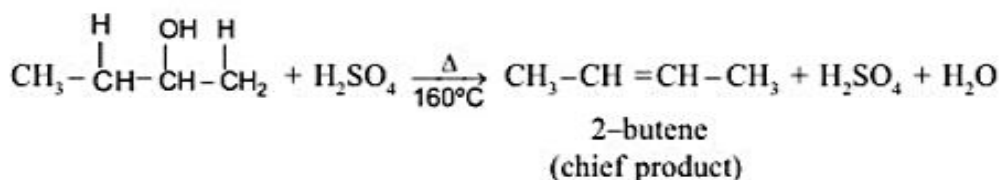
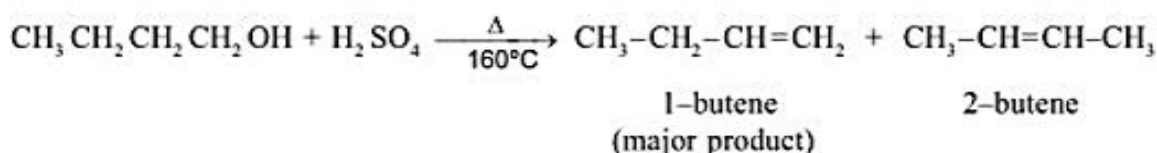
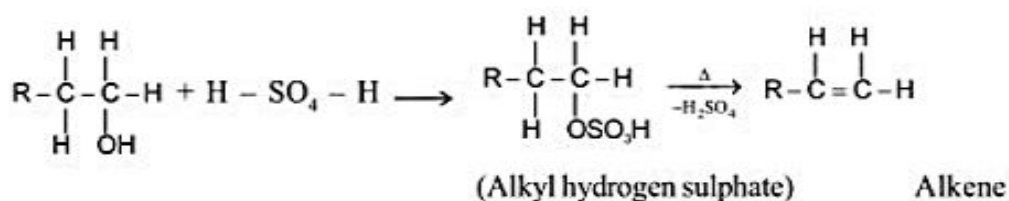


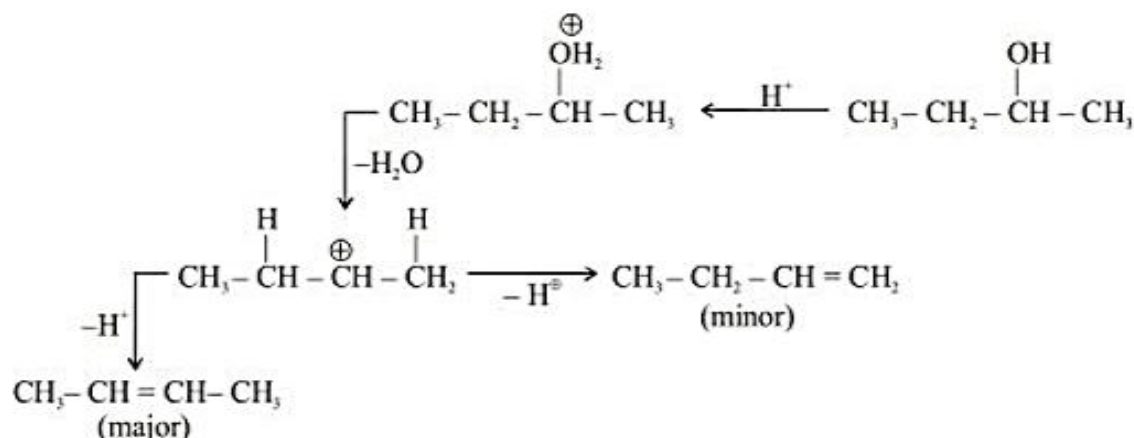
**Note :** Alkene is not formed from 1,3 dihalides. Cyclo alkanes are formed by dehalogenation of it.  
For eg.



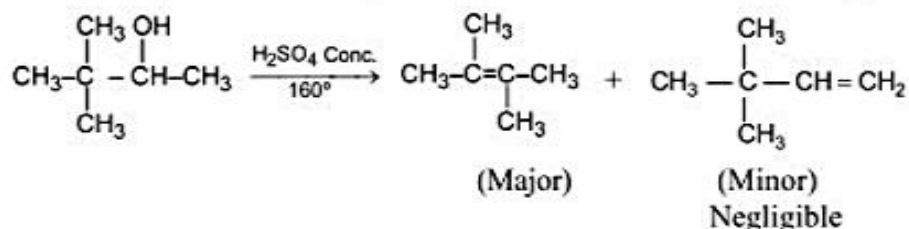
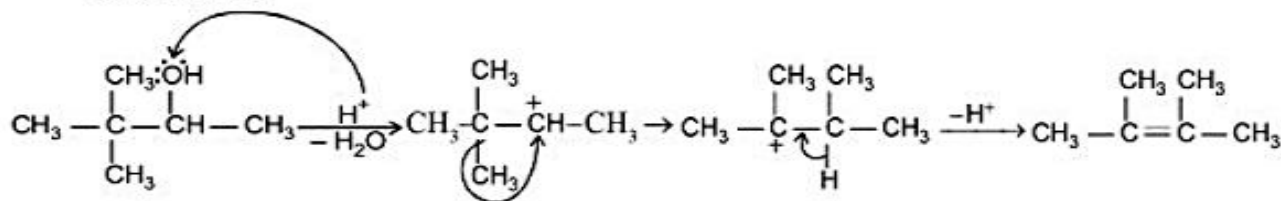
### From Alcohols

When alcohol is heated with conc.  $\text{H}_2\text{SO}_4$  at about  $160^\circ\text{C}$ , alkenes are formed after dehydration.



**Mechanism :-**

**Note :** Since the mechanism proceeds via-  $\text{C}^+$  ion therefore *rearrangement* is also possible eg.:

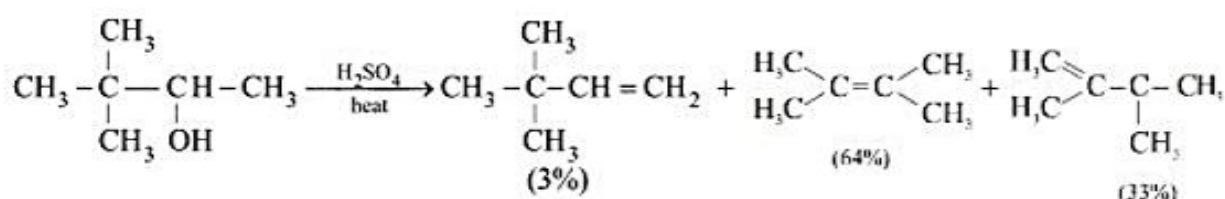
**Mechanism :****Characteristics of dehydration of alcohol**

- (1) Since the carbocation is formed as an intermediate in the R.D.S. of dehydration of alcohol The relative reactivity of alcohols decreases in the order.  
Tertiary > Secondary > Primary
- (2) Since the R.D.S. is reversible it is necessary to remove the  $\text{H}_2\text{O}$  molecule produced in the reaction. Therefore in experimental condition conc.  $\text{H}_2\text{SO}_4$  is added in a regular interval.
- (3) For dehydration, different dehydrating agent like  $\text{Al}_2\text{O}_3$ ,  $\text{ThO}_2$  can also be employed.
- (4) Rearrangement of carbocation can take place.
- (5)  $-\text{OH}$  is not a good leaving group, in alcohols so turn it into a good leaving group, it is converted into  $-\text{H}_2\text{O}$  by protonation
- (6)  $\text{H}_2\text{O}$  is a good leaving group.

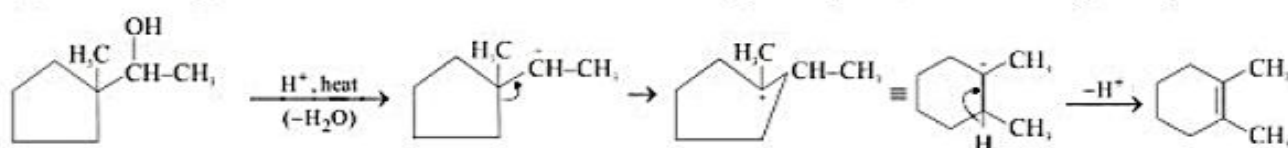
**Rearrangement in Alcohol Dehydration**

- (1) Some alcohols undergo dehydration to form alkene having carbon skeleton different from those of the starting alcohol.
- (2) This is due to rearrangement of carbocation formed in the reaction to more stable carbocation.
- (3) An example of alcohol dehydration that is accompanied by rearrangement is.



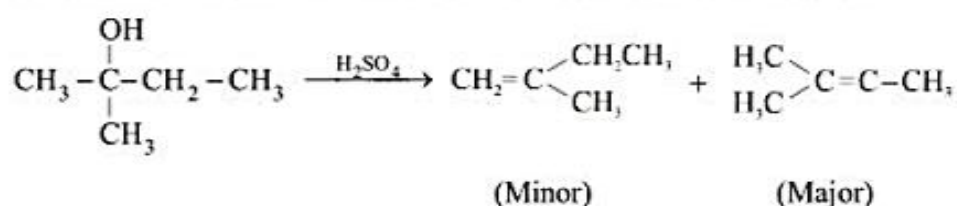


- (4) Percent yield of alkenes formed from rearranged carbocation is greater than the percent yield of alkene obtained from unrearranged carbocation.
- (5) Rearrangement of carbocations can also lead to a change in ring size, as the following example shows



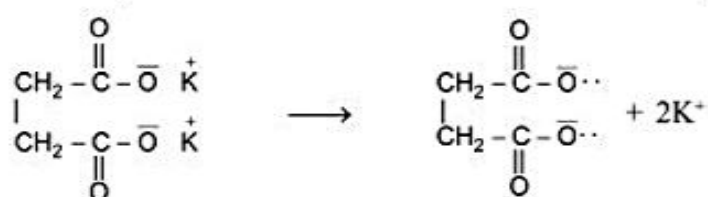
### Regioselectivity in alcohol dehydration :

1. In alcohols such as 2-methyl-2-butanol, dehydration can occur in two different directions to give alkenes that are constitutional isomers.
2. More substituted alkene forms the major product and is called Saytzeff alkene or Zaitsev alkene.
3. Less substituted forms the minor product and is called Hofmann's alkene.

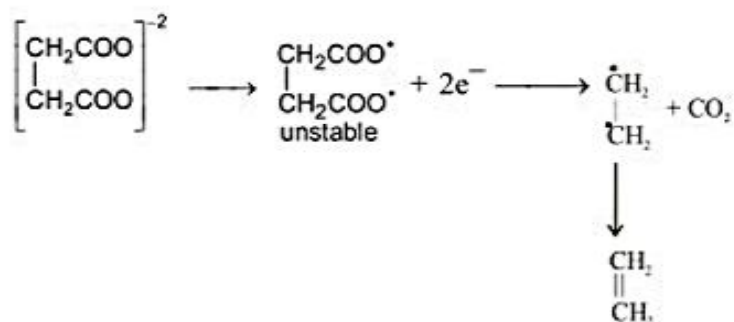


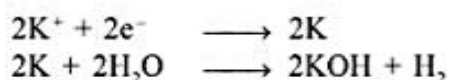
### Kolbe's Synthesis

When aqueous solution of K or Na succinate is electrolysed, ethylene is released at anode.



### At Anode

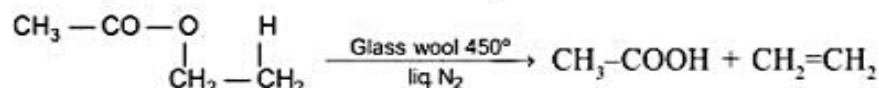


**At Cathode**

**Note** – If we use methyl succinic acid as reactant then propylene is formed.

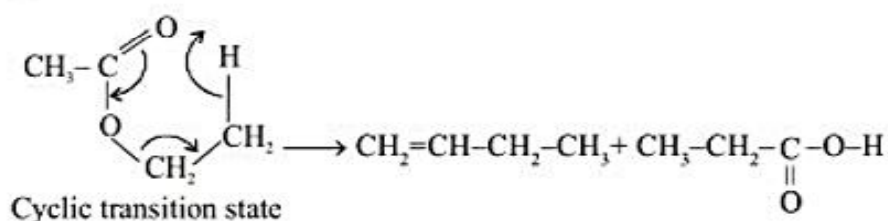
**From Esters**

When esters are heated in presence of liq.  $N_2$  and glass wool, then alkyl part of ester converts into respective alkene while alkanoate part of ester is converted into respective acid.

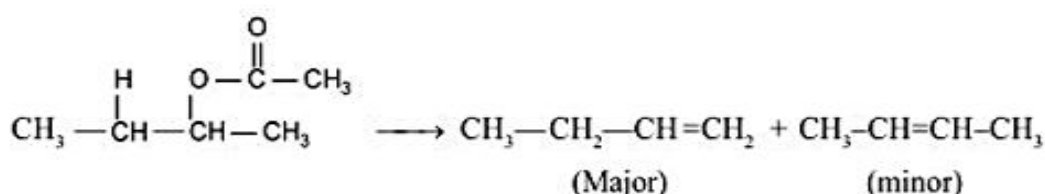


The reaction is called as 'Pyrolysis of Ester'.

**Mechanism :** Pyrolysis of Ester is a type of  $E_1$  elimination which proceed via *cyclic T.S.* that is why the product becomes 'cis'



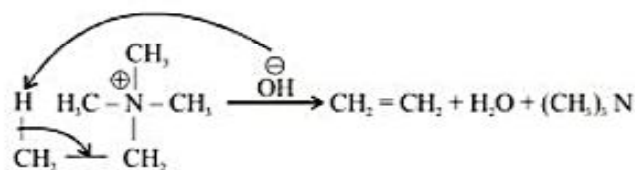
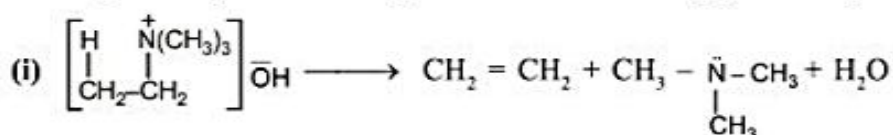
\* It is interesting to note that, in this case major product is 1-alkene in the comparison to 2-alkene.

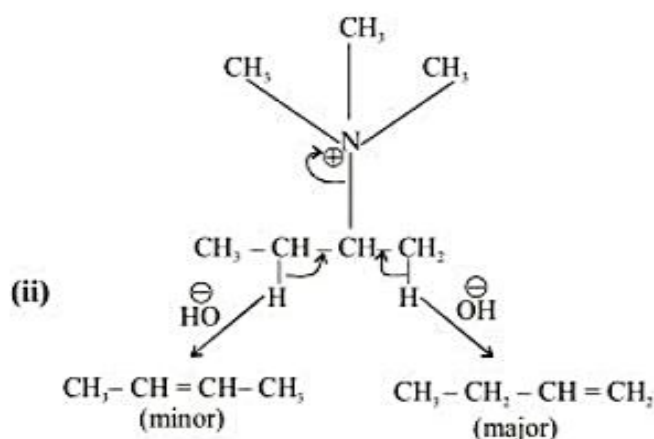


Major product is obtained by removal of  $-H$  from less hindered carbon.

**From quaternary ammonium hydroxide**

When quaternary ammonium hydroxide is heated strongly it decomposes to give alkene. eg.

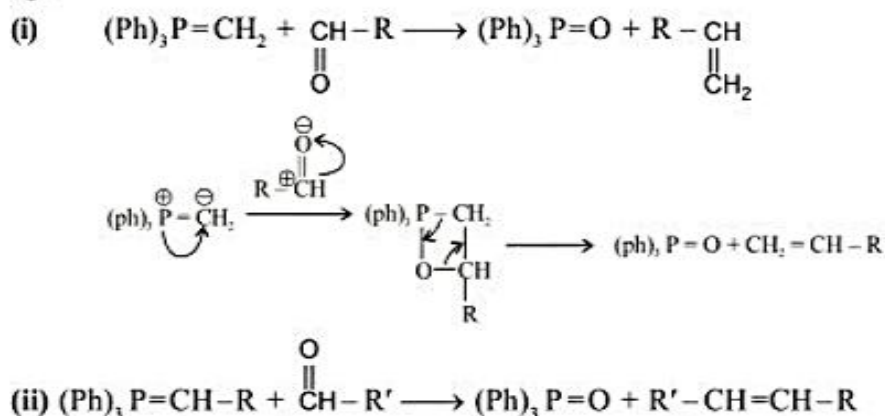




This elimination is called **Hoffman's elimination**. It is markable that in this reaction more acidic H is preferably eliminated.

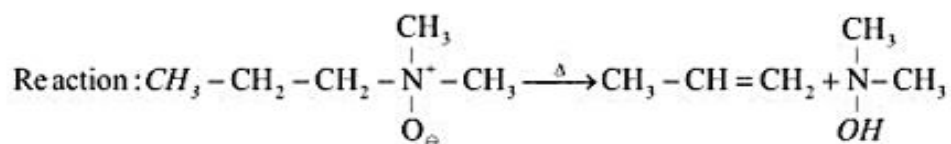
### The wittig reaction

In this reaction methylene triphenyl phosphorane is reacted with carbonyl compound to give alkene.  
eg. :

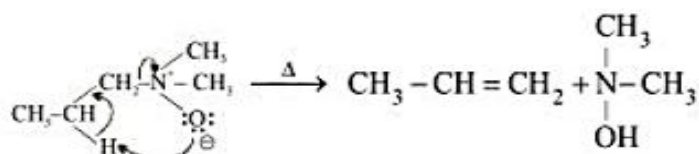


### The Cope Elimination :

Tertiary amine oxide undergoes the elimination of a dialkylhydroxyamine when they are heated. This reaction is called the Cope elimination.



### Mechanism :



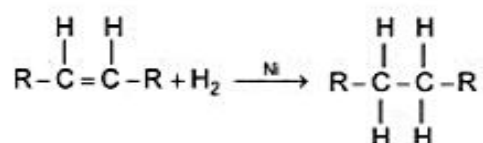
## PHYSICAL PROPERTIES

- (i) From  $C_2-C_4$  they are colourless, odourless gases, from  $C_5-C_{17}$  they are colourless liquids,  $C_{18}$  onwards alkenes are solids.
- (ii) Alkenes are practically insoluble in water because they cannot form hydrogen bonds with  $H_2O$  molecule. They dissolve freely in organic solvents like benzene, chloroform,  $CCl_4$  petroleum ether, etc. ( Like dissolves like )
- (iii) B.P and M.P. decreases with increasing branches in alkene.
- (iv) The melting points of cis isomers are lower than trans isomers because cis isomer is less symmetrical than trans. Thus trans packs more tightly in the crystal lattice and hence has a higher melting point.
- (v) The boiling points of cis isomers are higher than trans isomers because cis-alkenes has greater polarity (Dipole moment) than trans one.
- (vi) These are lighter than water.
- (vii) The increase in branching in carbon chain decreases the boiling point among isomeric alkenes.

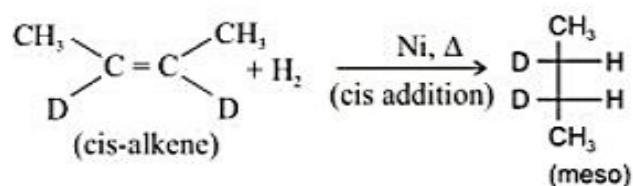
## CHEMICAL REACTIONS

The main reactions of alkene are electrophilic addition reaction

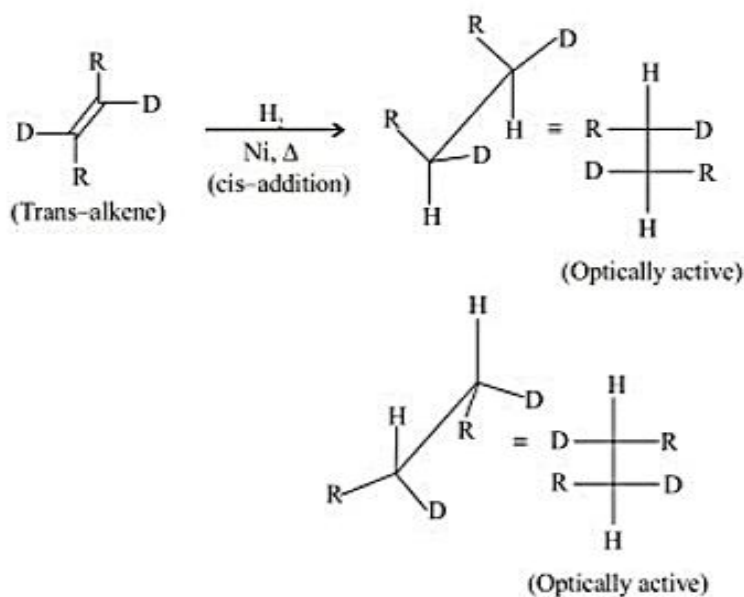
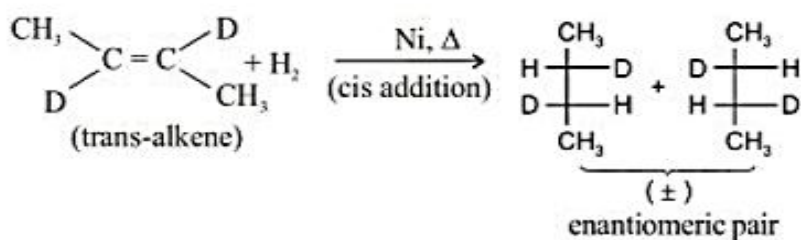
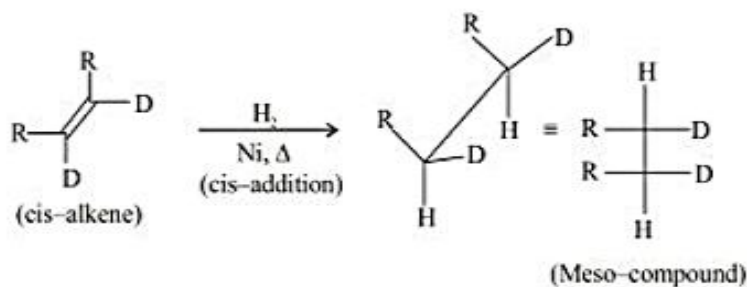
### Reaction with Hydrogen –



**Mechanism :** The reaction takes place at the surface of Ni, therefore the addition is cis addition.  
eg :-





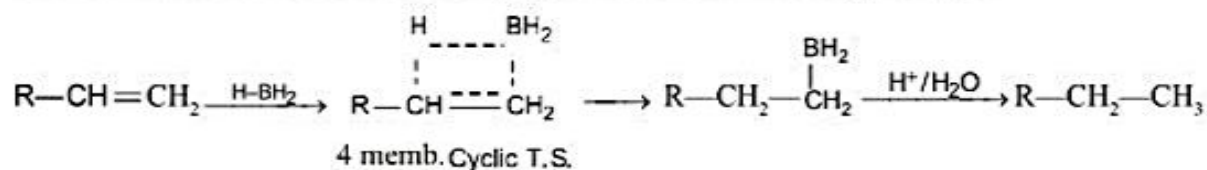


**Note :** Hydrogenation (catalytic hydrogenation) of alkene is a cis addition and is an exothermic reaction. Thus the heat evolved decreases with increasing stability of alkene.

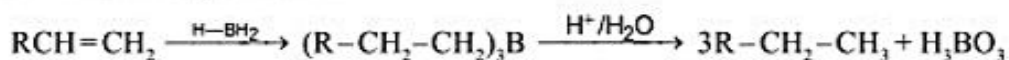
**Remember,** Stability of alkene depends upon hyperconjugation and type of geometrical isomerism

#### Reduction of alkene via hydroboration

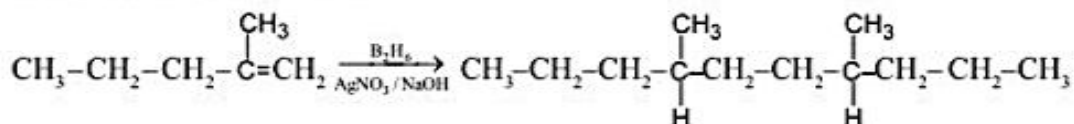
(i) Alkene can be converted in to alkane by hydroboration followed by protolysis



This reaction is also represented as

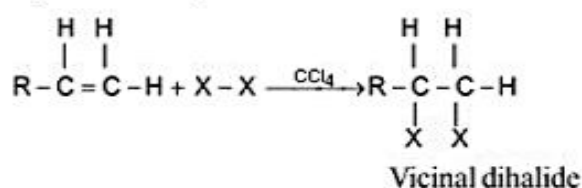


- (ii) Alkene can be converted into alkane by hydroboration followed by treatment with  $\text{AgNO}_3 + \text{NaOH}$ . This method gives coupling.



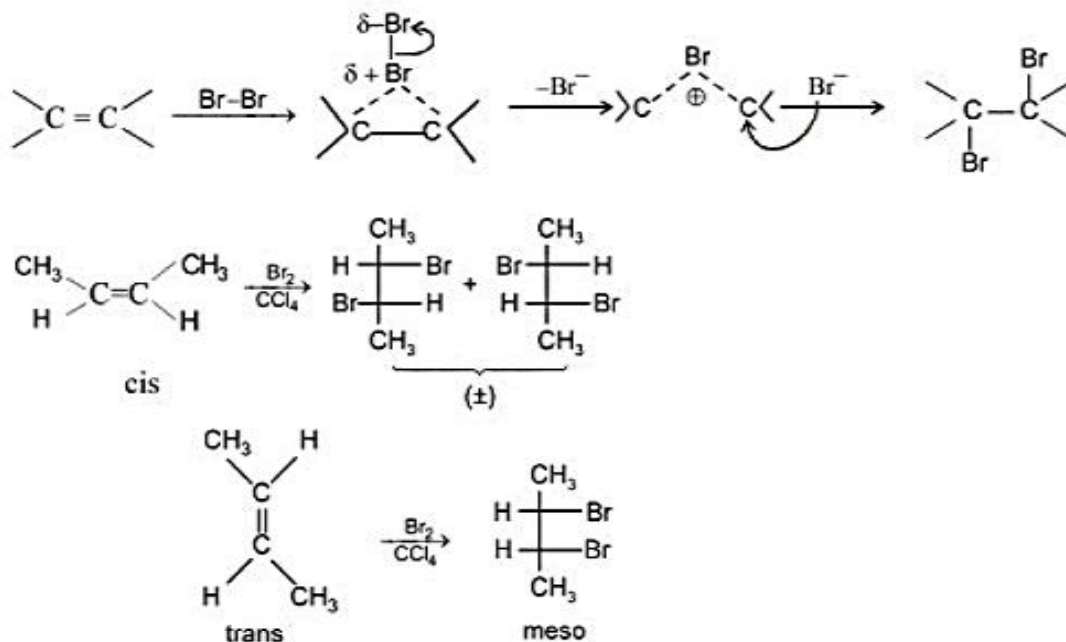
### Halogenation –

In presence of polar medium alkene form vicinal dihalide with halogen.



Order of reactivity of halogens is :  $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$

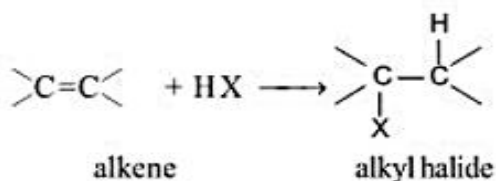
**Mechanism :** It is an electrophilic addition by molecular attack in which the addition takes place in trans manner.



**Note :** For suitable condition

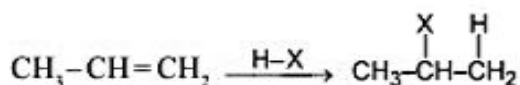
- (i) Cis addition on cis form results meso
- (ii) Cis addition on trans form results (±)
- (iii) Trans addition on cis form results (±)
- (iv) Trans addition on trans form results meso.

## Reaction with HX (Hydrohalogenation) –

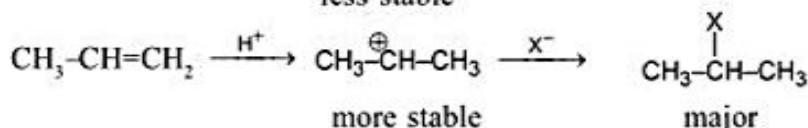
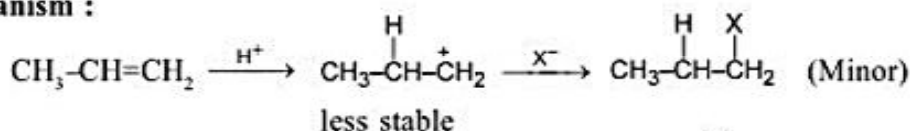


### Markovnikoff's Rule

When an unsaturated unsymmetrical hydrocarbon reacts with HX then halogen goes on that unsaturated carbon which has minimum number of hydrogen atom. Mechanism of the reaction is based on  $\text{—C}^{\oplus}\text{—}$ .



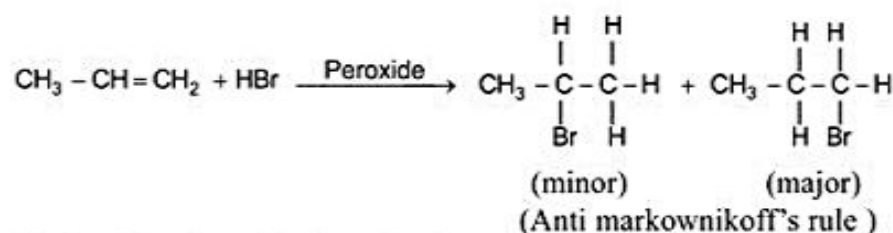
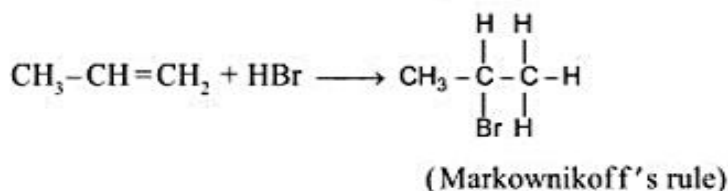
### Mechanism :



- (i) Formation of Carbocation is Rate determining step.
- (ii) Rearrangement of carbocation to more stable carbocation can occur to form a more stable product.
- (iii) Regiochemistry - Markownikoff's Addition of HX.  
Addition of HX on unsymmetrical alkenes ( $\text{R—CH=CH}_2$ ) takes place according to Markownikoff's rule which states that, "the negative part of addendum is added on the carbon atom carrying lesser number of hydrogen atoms".
- (iv) Reactivity order of different hydrogen halide towards addition  
 $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$

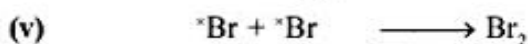
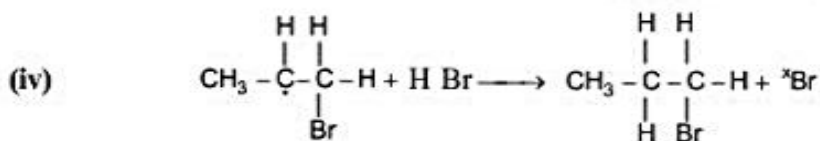
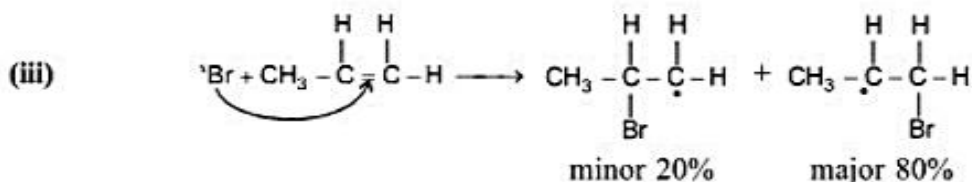
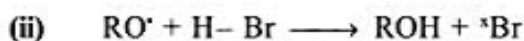
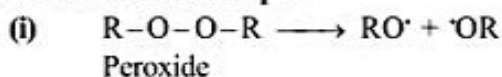
### Anti Markownikoff's Principle / Kharasch Effect / Peroxide Effect –

To understand antimarkownikoff's principle let us consider the following reactions



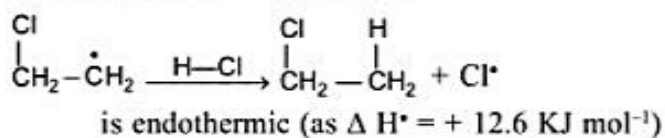
It is based on free radical mechanism.

## (a) Mechanism Concept –

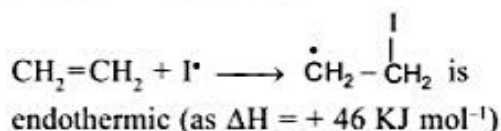


**Note :** It is interesting to note that anti markovnikov addition in the presence of peroxide is not applicable for HCl and HI

(i) In the case of H – Cl, the step



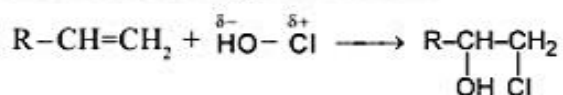
(ii) In the case of H – I, the step



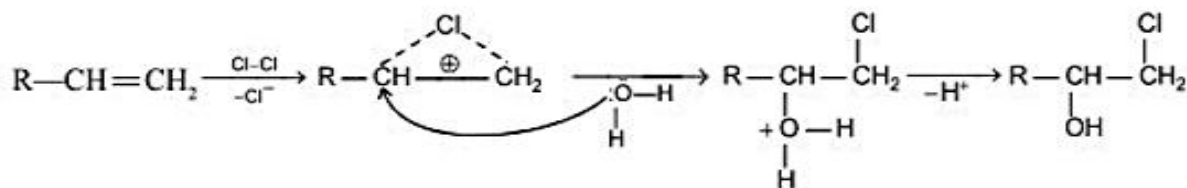
But in the case of HBr both of the steps are exothermic, which results spontaneous reaction.

\*  $CCl_4$ ,  $CBrCl_3$  etc. can also be added to alkene in anti markovnikov manner.

### Reaction with Hypohalous Acid –

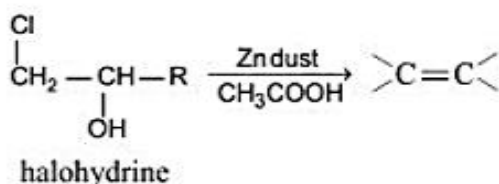
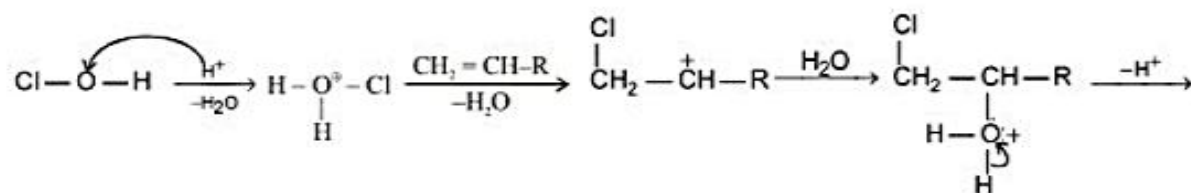


(i) When chlorine water or bromine water is used.



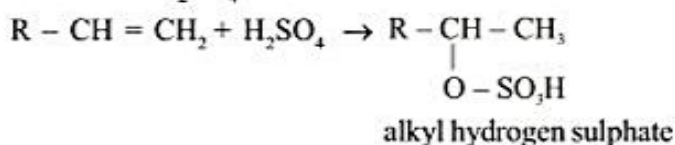


(ii) When aq. solution of HOCl is added in the presence of strong acid.

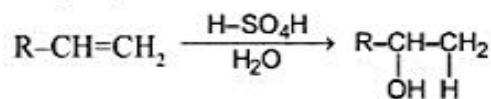


### Reaction with $\text{H}_2\text{SO}_4$ -

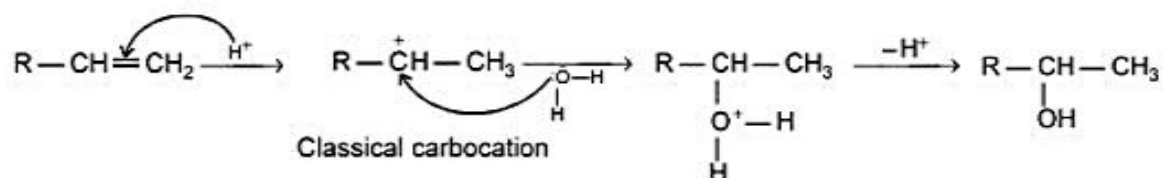
(a) With conc.  $\text{H}_2\text{SO}_4$



(b) With dil.  $\text{H}_2\text{SO}_4$

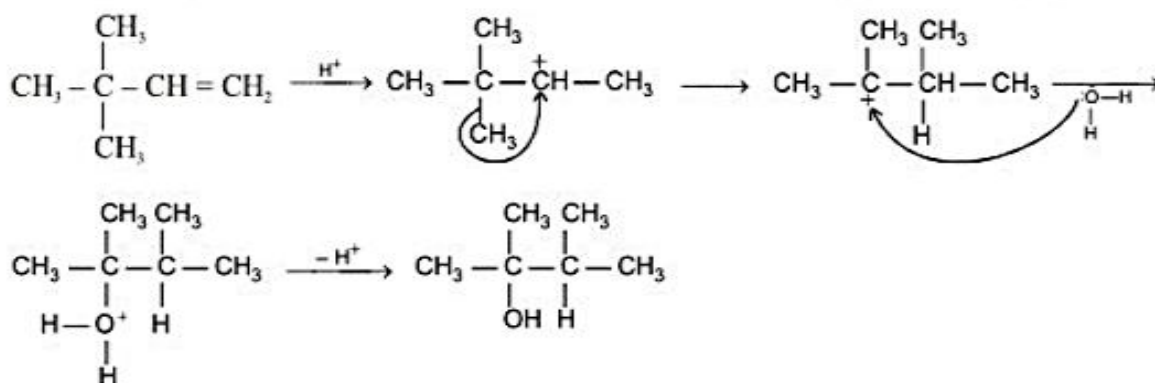


### Mechanism:

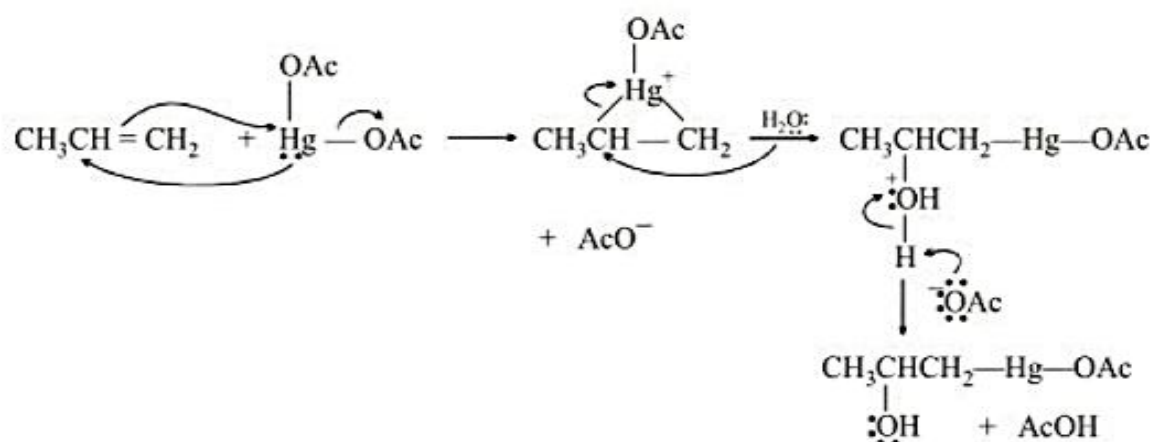


\* The hydration of alkene is not stereoselective, as in the case of HCl addition. This fact can be explained on the basis of classical carbon cation formation.

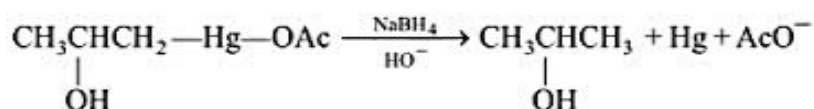
\* Since hydration proceeds via carbocation intermediate therefore rearrangement is always probable.



\* Rearrangement, however, may be avoided by treatment of alkene by *oxymmercuration-demercuration method*

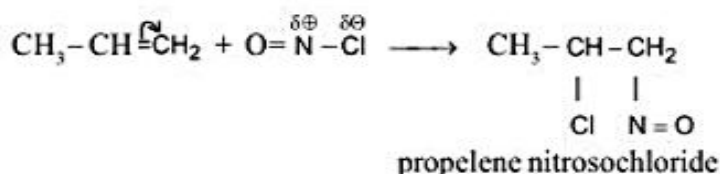
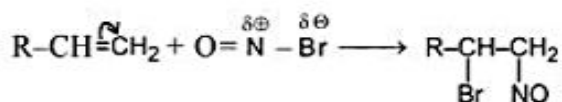
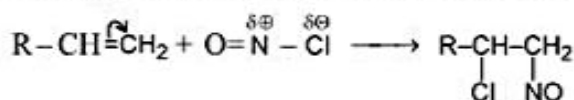


Sodium borohydride ( $\text{NaBH}_4$ ) converts the carbon-mercury bond into a carbon-hydrogen bond. Because the reaction results in the loss of mercury, it is called demercuration.



### Addition of Nitrosyl halide –

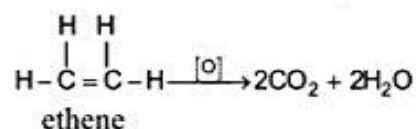
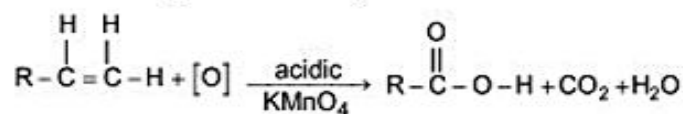
Alkene with nitrosyl bromide or nitrosyl chloride (**Tilden reagent**) react according to Markovnikoff's rule to give alkene nitrosobromide and alkene nitrosochloride respectively.

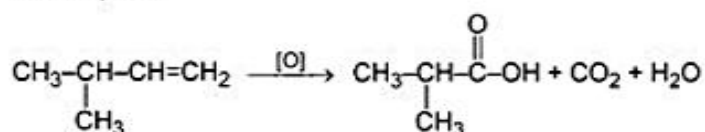
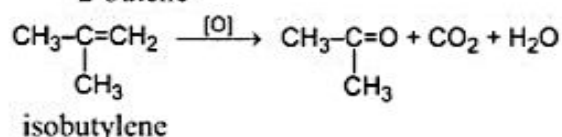
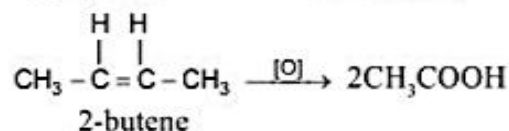
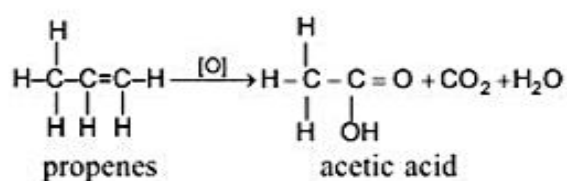


### Oxidation

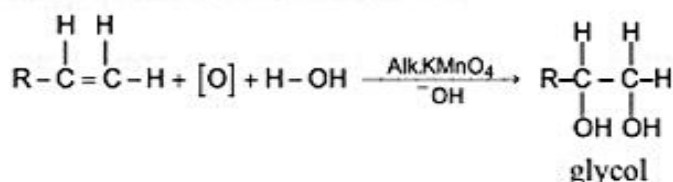
Oxidation is completed by the following ways.

**With Acidic  $\text{KMnO}_4$  / Hot  $\text{KMnO}_4$**

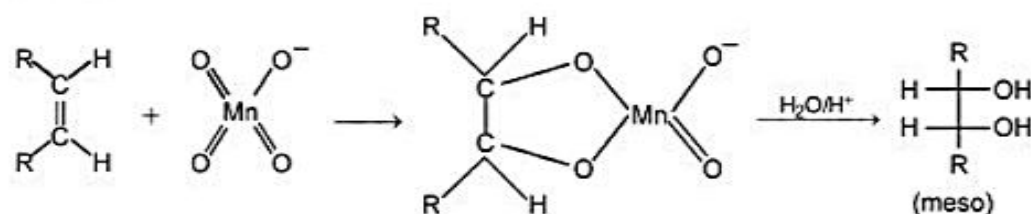




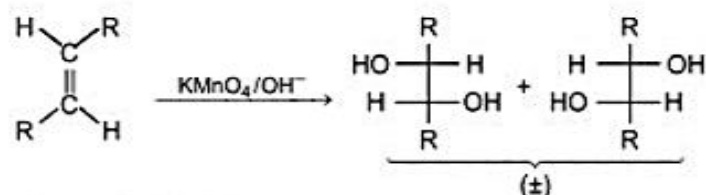
With alkaline  $\text{KMnO}_4$  / Bayer's reagent



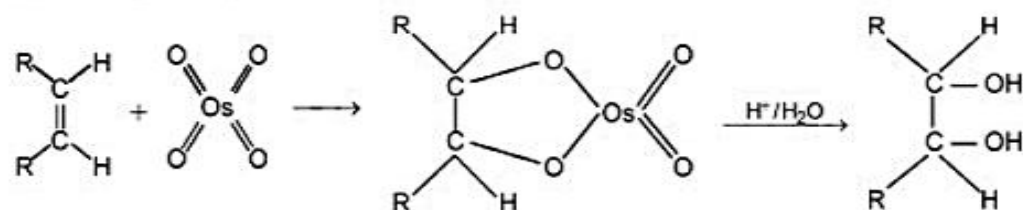
**Mechanism:** Hydroxylation by alkaline  $\text{KMnO}_4$  (Bayer's reagent) is cis addition and the mechanism is cyclic.

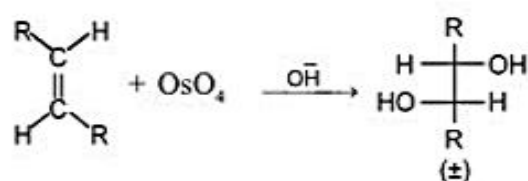


Similarly



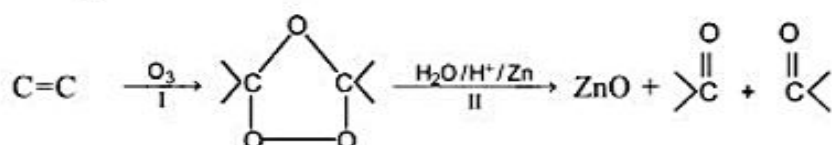
Hydroxylation by  $\text{OsO}_4$  :



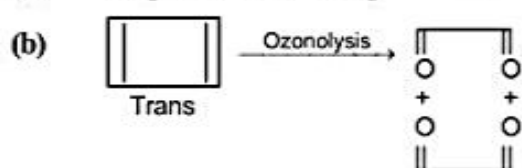
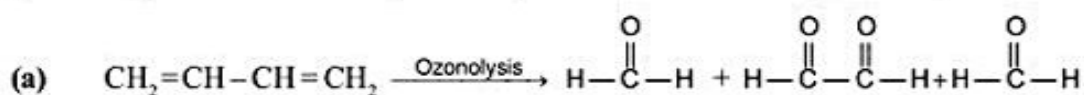
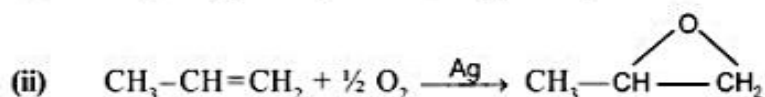
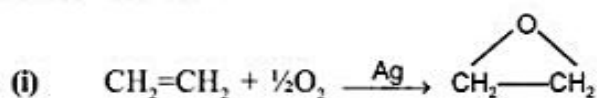
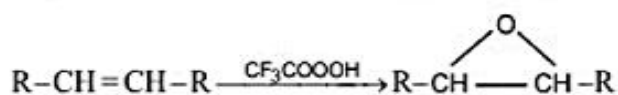
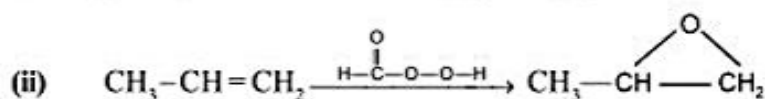
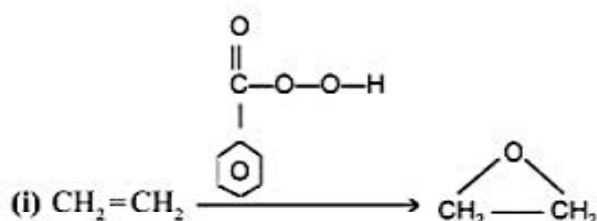
**Ozonolysis :-**

This is the two step reaction

- (i) Ozonide formation
  - (ii) decomposition of ozonide (reductive hydrolysis)
- eg:-



**Remember :** Ozonolysis gives oxidative cleavage of alkene to form two carbonyl group for each  $>\text{C}=\text{C}<$ . Whether it is in acyclic or cyclic or in aromatic compound. eg :-

**Epoxidation by  $\text{O}_2/\text{Ag}$** **Epoxidation by per acid**

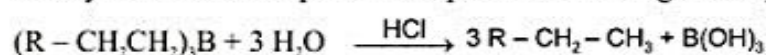


### Hydroboration

Alkene with borane hydride form an important compound called trialkyl borane.



- (a) Trialkyl borane is an important compound because it gives respective alkane on acidic hydrolysis.



- (b) It gives respective alcohol on alkaline hydrolysis



- (c) It gives 1° amine on alkaline hydrolysis with chloramine



- (d)  $(R-CH_2CH_2)_3B \xrightarrow[NaOH]{AgNO_3} 3R-CH_2-CH_2-CH_2-CH_2-R$

- (e) In the overall hydroboration-oxidation reaction, three moles of alkene react with one mole of  $BH_3$  to form three moles of alcohol.

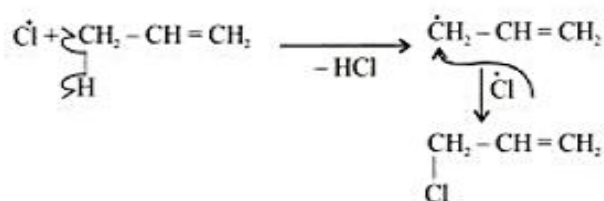
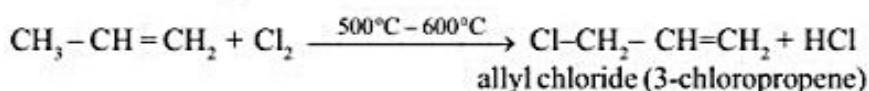
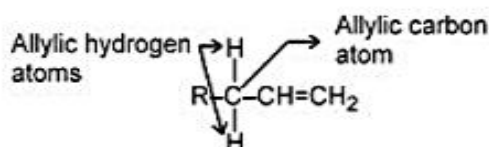
- (f) Because carbocation intermediates are not formed in the reaction carbocation rearrangement do not occur.

- (g) Regiochemistry Anti-markownikoff's Addition of water.

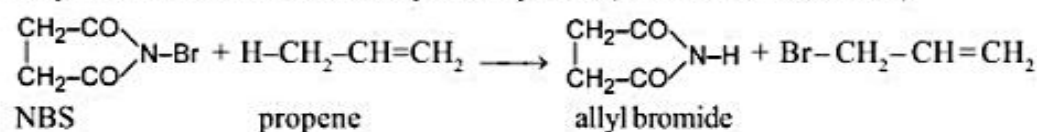
- (h) Alkyl boranes undergo coupling by means of silver nitrate in the presence of NaOH at 25°C. Higher alkanes are the products of this reaction.

### Allylic substitution reaction –

- (a) Except ethene other higher alkene having allyl hydrogen when treated with chlorine or bromine 'α' H is substituted.



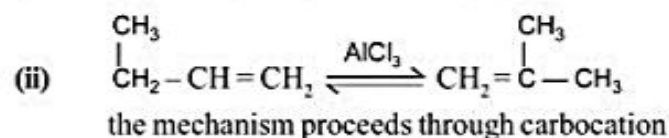
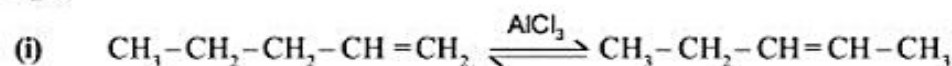
- (b) Allylic bromination can be easily done by NBS (N-bromo succinamide)



#### Isomerisation :-

Alkenes isomerise when heated at high temperature or at lower temperature in the presence of various catalysts as  $\text{AlCl}_3$

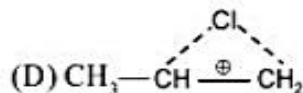
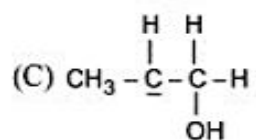
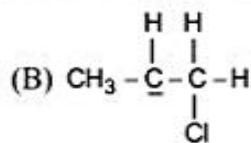
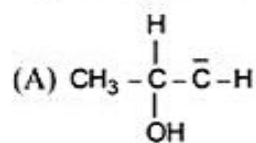
eg :-



### MCQ

- Q.1  $\text{R-CH=CH}_2 \xrightarrow[\text{C}_2\text{H}_5\text{OH}]{\text{Na/NH}_3(\text{l})} \text{RCH}_2\text{CH}_3$  is called  
(A) Clemmensen's reduction (B) Fisher-Spier reduction  
(C) Birch reduction (D) Arndt-Eistert reduction
- Q.2 What would be the product when 2-pentene reacts with  $\text{HBr}$  –  
(A) 2-bromo pentane (B) 3-bromo pentane (C) Both A and B (D) 1-bromo pentane
- Q.3 What would be the product when ethene is oxidised with ozone and forms ozonide which is hydrolysed in the presence of  $\text{Zn}$  and acetic acid?  
(A)  $\text{H}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{H}$  (B)  $\text{CH}_3\text{OH}$  (C)  $\text{H}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{OH}$  (D)  $\text{H}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{H}$
- Q.4 What would be the product when propene reacts with chlorine in presence of  $\text{CCl}_4$   
(A)  $\begin{array}{c} \text{H} \quad \text{H} \\ | \quad | \\ \text{CH}_3-\text{C}-\text{C}-\text{H} \\ | \quad | \\ \text{Cl} \quad \text{Cl} \end{array}$  (B)  $\text{Cl-CH}_2\text{-CH=CH}_2$   
(C)  $\begin{array}{c} \text{H} \quad \text{H} \\ | \quad | \\ \text{CH}_3-\text{C}=\text{C}-\text{Cl} \end{array}$  (D)  $\begin{array}{c} \text{H} \quad \text{H} \\ | \quad | \\ \text{CH}_3-\text{C}-\text{C}-\text{H} \\ | \quad | \\ \text{Cl} \quad \text{H} \end{array}$
- Q.5 Propene on reaction with methylene iodide in presence of  $\text{Zn-Cu}$  couple gives :  
(A) Cyclopropane (B) Cyclopropane  
(C) Methyl Cyclopropane (D) Cyclobutene

Q.6 Propene +  $\text{HOCl} \rightarrow \text{A} \rightarrow \text{Final product}$ . In the above reaction A will be



Q.7 In hydroboration it is evident that in the overall reaction a molecule of a water has been added to propene and the addition is :

- (A) According to markownikoff's rule (B) Contrary to Markownikoff's rule  
(C) Not concerned with markownikoff's rule (D) None of above

Q.8 NBS react with 1-butene to give –

- (A) 3-bromobutene-1 (B) 1,2-dibromobutane (C) 1-bromobutene (D) 1,2-dibromobutene-1

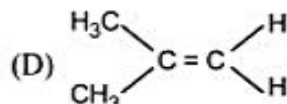
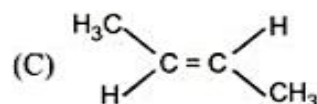
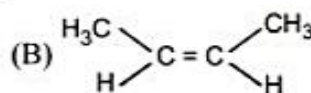
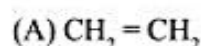
Q.9 Isobutane reacts with the following to form isooctane :

- (A) Isobutylene (B) n-Butene (C) n-Pentene (D) Isopentene

Q.10 Reaction of alkene and peracid gives oxirane. This reaction is named as –

- (A) Peroxidation (B) Oxidation (C) Priles chaiev (D) None

Q.11 The compound which reacts with HBr obeying Markownikov's rule is -



Q.12 Alkene and alkyne gives following types of polymerisation –

- (A) Addition (B) Condensation (C) Substitution (D) Replacement

Q.13 Cyclic osmium ester of alkene after reacting with aqueous solution of sodium bisulphite gives –

- (A) Diol (B) Cis-diol (C) Trans-diol (D) Salt

Q.14 The minimum number of C atoms required to be present in an optically active alkene are:

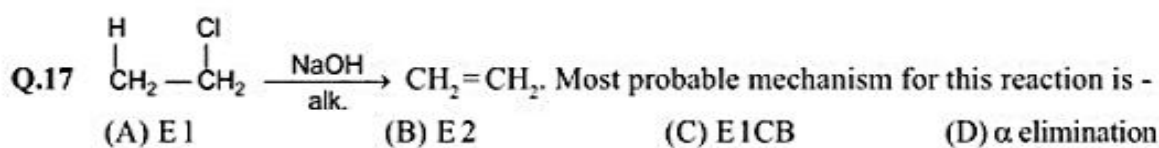
- (A) 4 (B) 6 (C) 8 (D) 10

Q.15 Chloroethane reacts with alcoholic KOH to form –

- (A) Propyl chloride (B) Ethyl chloride (C) Ethene (D) None

Q.16 The synthesis of ethene from electrolysis of an aqueous solution of potassium succinate is known as:

- (A) Faradays electrolysis (B) Kolbe - Schmidt reaction  
(C) Hoffmann's rearrangement (D) Kolbe's electrolytic Synthesis



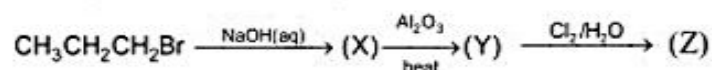
Q.18  $\text{RCH} = \text{CH}_2$  can be obtained by :

- (A)  $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$  and  $(\text{C}_6\text{H}_5)_3\text{P} = \text{CH}_2$  (B) By heating  $\text{RCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$   
 $\downarrow$   
 $\text{O}$   
 (C) By heating  $\text{RCH}_2\text{CH}_2\text{OCOCH}_3$  (D) All of these

Q.19 If we take ethylidene chloride and isopropylidene chloride with zinc dust then product will be -

- (A) 2-butene  
 (B) 2-butene + 2,3-dimethyl-2-butene  
 (C) 2-methyl-2-butene  
 (D) 2-butene, 2-methyl-2-butene, 2,3-dimethyl-2-butene

Q.20 Identify 'Z' in the following reaction series,



- (A) Mixture of  $\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_2 \\ | \quad | \\ \text{Cl} \quad \text{Cl} \end{array}$  and  $\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_2 \\ | \quad | \\ \text{OH} \quad \text{Cl} \end{array}$   
 (B)  $\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_2 \\ | \quad | \\ \text{OH} \quad \text{Cl} \end{array}$   
 (C)  $\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_2 \\ | \quad | \\ \text{Cl} \quad \text{OH} \end{array}$  (D)  $\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_2 \\ | \quad | \\ \text{Cl} \quad \text{Cl} \end{array}$

### ANSWERS KEY

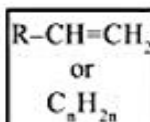
Q.1	C	Q.2	C	Q.3	A	Q.4	A
Q.5	C	Q.6	D	Q.7	B	Q.8	A
Q.9	A	Q.10	C	Q.11	D	Q.12	A
Q.13	B	Q.14	B	Q.15	C	Q.16	D
Q.17	B	Q.18	D	Q.19	D	Q.20	B



# REACTION CHART FOR ALKENES

## GMP

- (1)  $R-H \xrightarrow{\text{Pyrolysis}}$
- (2)  $R-C=CH \xrightarrow[200-300^\circ C]{Ni, H_2}$
- (3)  $R-CH_2-CH_2-X \xrightarrow[-HX]{alc. KOH}$
- (4)  $R-CH_2-CH \begin{smallmatrix} \nearrow X \\ \searrow X \end{smallmatrix} \xrightarrow[-X_2]{Zn dust}$  for higher alkene
- (5)  $\begin{array}{c} R-CH-CH_2 \\ | \quad | \\ X \quad X \end{array} \xrightarrow{Zn dust}$
- (6)  $CH_2=CHCl \xrightarrow{CuR_2}$
- (7)  $R-CH_2-CH_2-OH \xrightarrow[-H_2O]{conc. H_2SO_4}$
- (8)  $\begin{array}{c} R-C-O-CH_2-CH_2-R \\ || \\ O \end{array} \xrightarrow{\text{Pyrolysis}}$
- (9)  $\begin{array}{c} RCHCH_2COOK \\ | \\ COOK \end{array} \xrightarrow{\text{Kolbe's electrolytic synthesis}}$
- (10)  $(RCH_2CH_2)_4 N^+ OH^- \xrightarrow{\Delta}$



## GR

- (1)  $\xrightarrow[200-300^\circ C]{H_2, Ni} R-CH_2-CH_3$
- (2)  $\xrightarrow{X_2} R-CHX-CH_2X$
- (3)  $\xrightarrow{HX} R-CHX-CH_3$
- (4)  $\xrightarrow{HBr, Peroxide} R-CH_2-CH_2Br$
- (5)  $\xrightarrow{HOCl} R-CH(OH)-CH_2Cl$
- (6)  $\xrightarrow[+H_2O]{dil. H_2SO_4} R-CH_2(OH)-CH_3$
- (7)  $\xrightarrow[Ag, 300^\circ C]{1/2 O_2} \begin{array}{c} R-CH-CH_2 \\ | \quad | \\ O \end{array}$
- (8)  $\xrightarrow{+CH_2N_2} \begin{array}{c} R-CH-CH_2 \\ | \quad | \\ CH_2 \end{array}$
- (9)  $\xrightarrow{BH_3} (RCH_2CH_2)_3B$
- (10)  $\xrightarrow[HCo(CO)_4]{CO+H_2} \begin{array}{c} R-CH-CH_3 \\ | \\ CHO \end{array} + \begin{array}{c} R-CH_2-CH_2 \\ | \\ CHO \end{array}$
- (11)  $\xrightarrow[\Delta]{O_2} CO_2 + H_2O$
- (12)  $\xrightarrow{OsO_4} \begin{array}{c} R-CH-CH_2 \\ | \quad | \\ OH \quad OH \end{array}$
- (13)  $\xrightarrow[1\% \text{ alkaline } KMnO_4]{\text{Bayer reagent}} \begin{array}{c} R-CH-CH_2 \\ | \quad | \\ OH \quad OH \end{array}$
- (14)  $\xrightarrow{\text{strong oxidant}} \begin{array}{c} R-C-OH \\ || \\ O \end{array} + CO_2 + H_2O$
- (15)  $\xrightarrow[\text{Priles-chalev's reaction}]{\text{Peracid}} \begin{array}{c} R-CH-CH_2 \\ | \quad | \\ O \end{array}$
- (16)  $\xrightarrow{O_3+H_2O} \begin{array}{c} R \\ \diagdown \\ C \\ || \\ O \end{array} + \begin{array}{c} H \\ \diagup \\ C \\ || \\ O \end{array} \begin{array}{c} H \\ \diagup \\ C \\ || \\ O \end{array} \begin{array}{c} H \\ \diagdown \\ C \\ || \\ O \end{array}$  Ozonolysis
- (17)  $\xrightarrow[200^\circ C \text{ high P}]{O_2} \text{Polyalkene}$
- (18)  $\xrightarrow[500^\circ C]{Cl_2} \text{Substitution product}$
- (19)  $\xrightarrow[200-300^\circ C]{Al_2(SO_4)_3} \text{Isomerisation}$
- (20)  $\xrightarrow{\text{acetic anhydride}} R-CH_2=CH-COCH_3$   
Methyl alkenyl ketone
- (21)  $\xrightarrow{\text{Alkane}} \text{Higher alkane}$

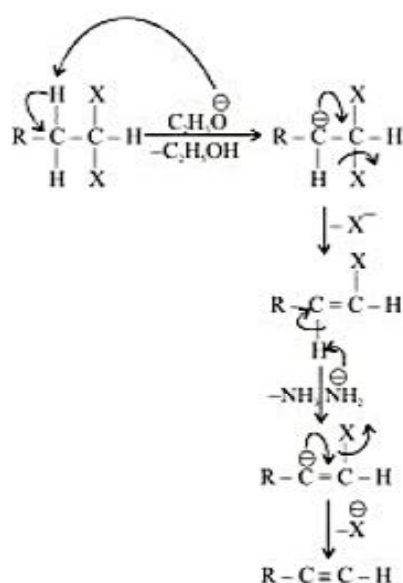
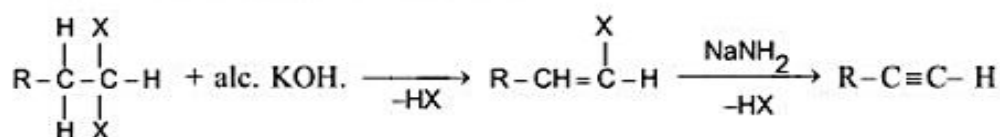
## ALKYNE

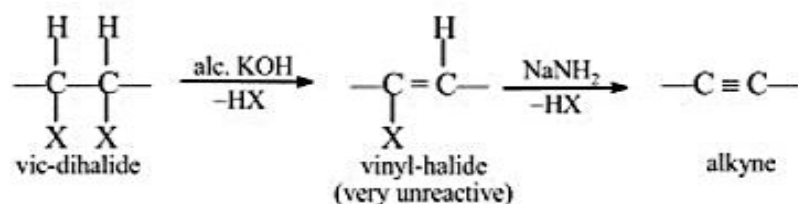
### GENERAL INTRODUCTION

- (1) The chemistry of the carbon-carbon triple bond is similar to that of the double bond. In this chapter, we see that alkynes undergo most of the reactions of alkenes, especially the additions and the oxidations. We also consider reactions that are specific to alkynes : some that depend on the unique characteristics of the  $C \equiv C$  triple bond, and others that depend on the unusual acidity of the acetylenic  $C-H$  bond.
- (2) Alkynes are hydrocarbons that contain carbon-carbon triple bonds. Alkynes are also called acetylenes because they are derivatives of acetylene, the simplest alkyne.
- (3) Bond angle in alkyne is  $180^\circ$ .
- (4) Their general formula is  $C_nH_{2n-2}$ .
- (5)  $C-C$  triple bond length is  $1.20 \text{ \AA}$ .
- (6)  $C-H$  bond length is  $1.08 \text{ \AA}$ .

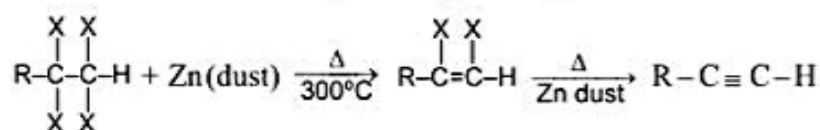
### Methods of Preparation

#### From Gem Dihalides (Dehydrohalogenation):

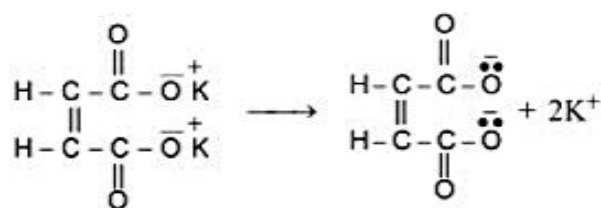


**From vicinal dihalides :**

The elimination of one molecule of hydrogen halide yields vinyl halide which is very unreactive. Under mild conditions, the dehydrohalogenation stops at vinylic halide stage but more vigorous conditions—like the use of a stronger base like amide ion ( $\text{NH}_2^-$ )—are required for alkyne formation.

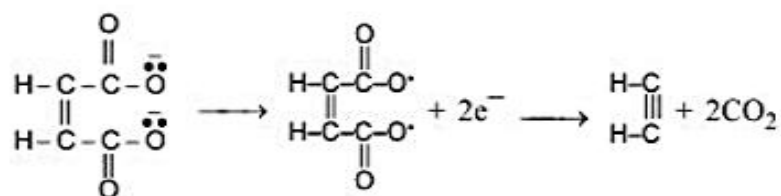
**From Tetrahaloalkanes (Dehalogenation) :**

In the above reaction it is necessary that the four halogen atoms must be attached at vicinal carbons. If they are attached at the two ends then the product cyclo alkene is obtained.

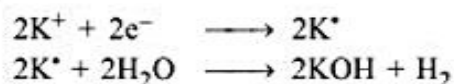
**From Kolbe's Synthesis :**

Potassium Malate

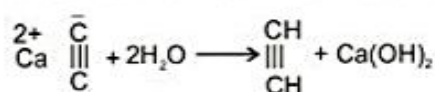
**At Anode :**



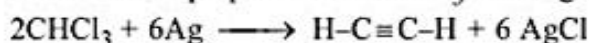
**At Cathode :**

**Laboratory method of preparation of Acetylene :**

(a) In laboratory acetylene is prepared by hydrolysis of calcium carbide.

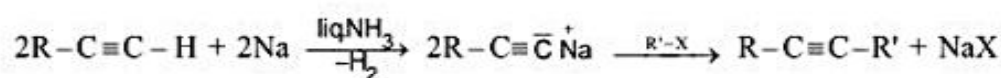
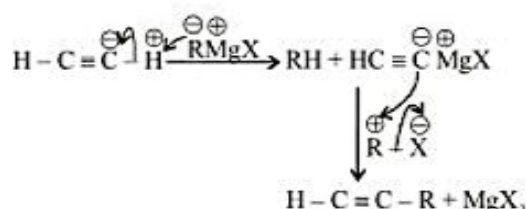
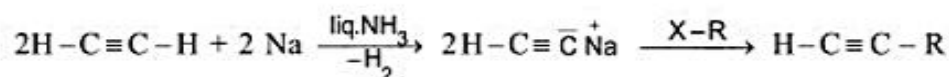


(b) It can also be prepared from  $\text{CHCl}_3$  with Ag dust.

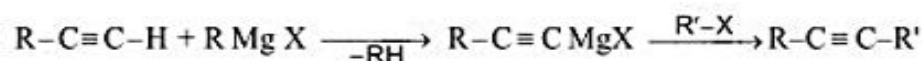
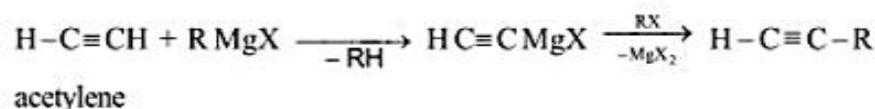


**From Alkynes : (To form higher Alkynes)**

**With Na :** When acetylene or 1- alkyne react with Na in presence of liq.  $\text{NH}_3$  then an intermediate compound sodium acetylide or sodium alkynide is formed which gives higher alkyne with alkyl halide.



**With Grignard reagent :** When acetylene or 1- alkyne react with GR then alkane and unsaturated GR is formed which further react with alkyl halide and form higher alkyne.

**PHYSICAL PROPERTIES**

- Alkynes are colourless, odourless and tasteless.
- Lower alkynes are partially soluble in  $\text{H}_2\text{O}$ . (It is due to its polarisability).
- Higher alkynes are insoluble in water due to more % of covalent character.
- Completely soluble in organic solvents.
- Melting point and boiling point increases with molecular mass and decreases with number of branches.
- Upto  $\text{C}_4$  alkynes are gaseous.  $\text{C}_5-\text{C}_{11}$  are liquid,  $\text{C}_{12}$  & above are solids.
- Pure acetylene is odourless and impure acetylene has odour like garlic. It is due to impurities of Arsene ( $\text{AsH}_3$ ) & Phosphine ( $\text{PH}_3$ ).

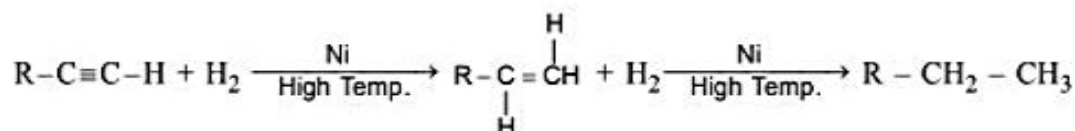


- (h) Acetylene & 1-alkyne are acidic in nature. It is due to greater electronegativity of  $sp$  hybridised 'C'.
- (i) Acetylene has two acidic hydrogen atoms. It can neutralise two equivalents of base at the same time. So it is also called as dibasic acid. But the base should be very stronger as  $^-NH_2$  or  $^-CH_3$  etc.

## CHEMICAL PROPERTIES

The chemical behaviour of alkynes is similar to that of alkenes. Alkynes form addition products with two or four univalent atoms or groups. They are generally less reactive than alkenes towards electrophilic addition reactions even though  $\pi$  electron density is higher in alkynes. This is because on moving from alkene to alkyne, the C—H bond has more of  $s$  character (33% in alkenes as compared to 50% in alkynes). Therefore, the  $\pi$ -electrons are more firmly held by carbon nuclei in alkynes and are thus less reactive to an electrophile.

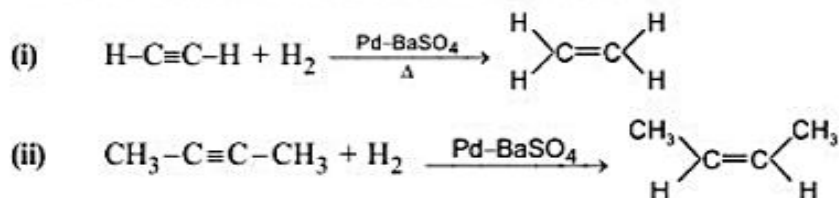
### Hydrogenation



The above reaction is called as **Sabatie Senderson's reaction**.

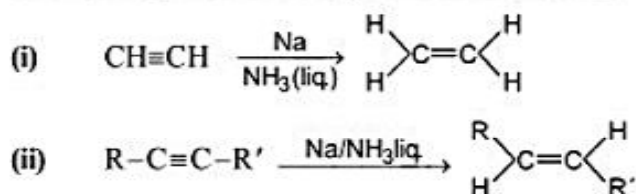
### Hydrogenation in the presence of lindlar's Catalyst :

Addition up to alkene takes place in cis manner.

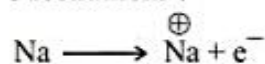


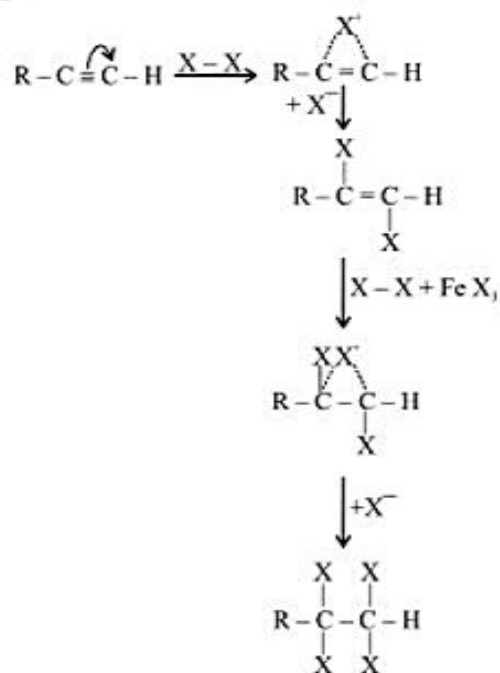
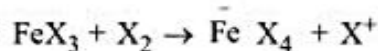
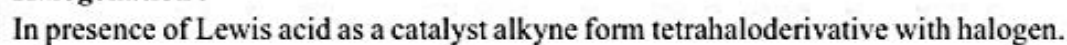
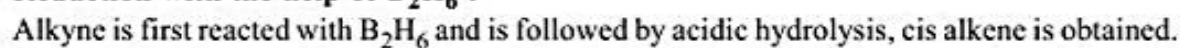
### Hydrogenation by Na + NH<sub>3</sub> (liq.) :

Addition upto alkene takes place in trans manner

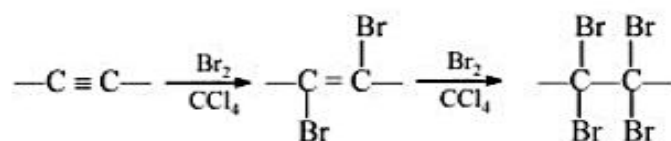


### Mechanism :





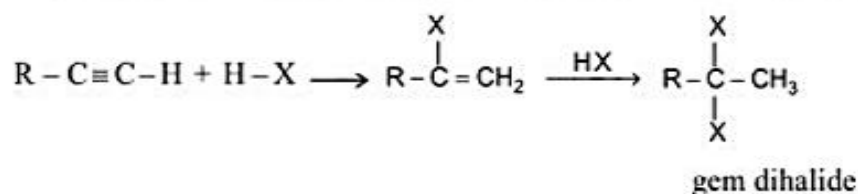
**Example :**



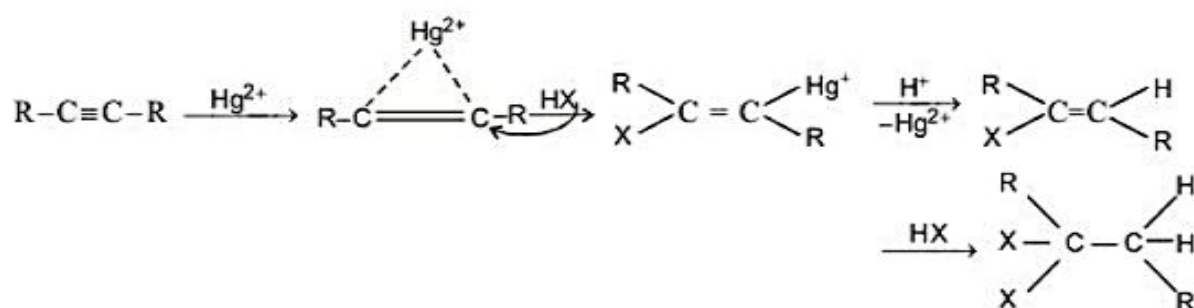
Alkynes add two molecules of  $\text{Br}_2$  in  $\text{CCl}_4$  and decoloration of bromine water is used to detect the presence of a double or triple bond.

**Reaction with HX (Hydrohalogenation) :**

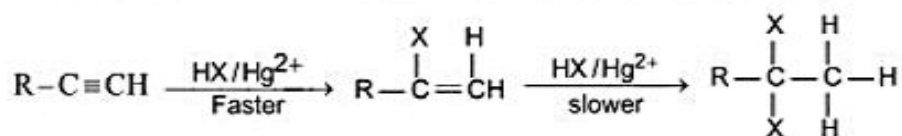
Alkyne form gem dihalide with HX because reaction follows markownikoff's 1st and 2nd rule both.



**Mechanism :** The reaction takes place in the presence of  $\text{Hg}^{2+}$  ion.

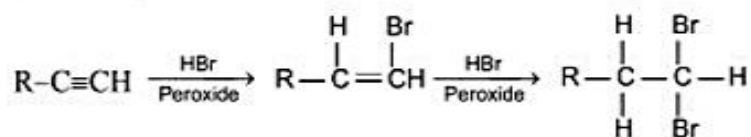


**Note :** (i) First step is faster than the second step among addition of two HX on alkyne.



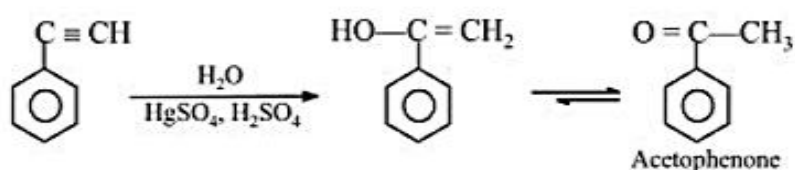
Slower rate of addition of 2nd molecule is caused by lower electron cloud density on  $\text{C}=\text{C}$ , due to  $-I$  effect of 'Cl'.

(ii) peroxide give same effect as in alkene

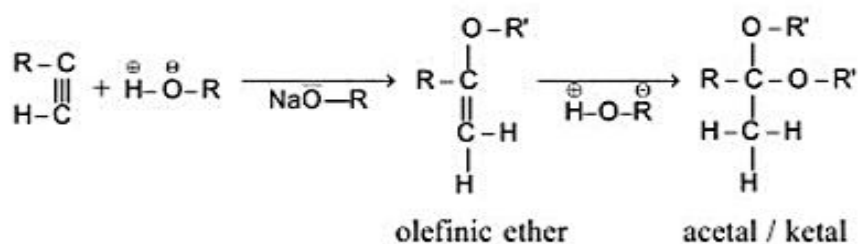






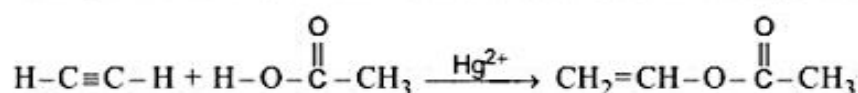


### Addition of alcohol



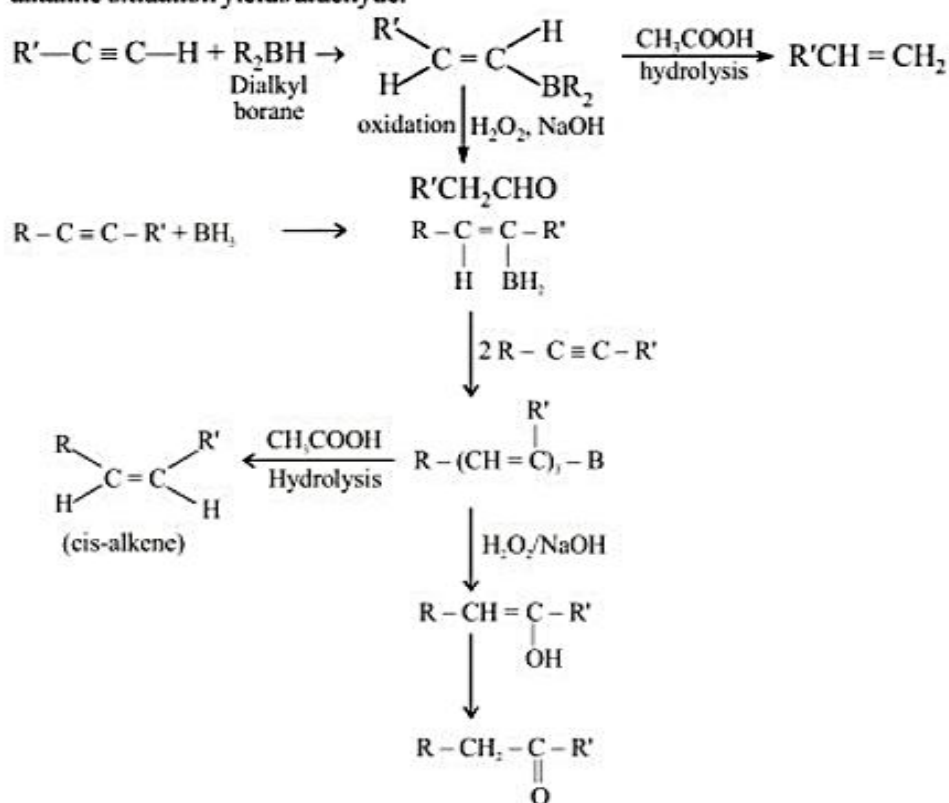
### Addition of carboxylic acid :

In the presence of  $\text{Hg}^{2+}$  unioxylation of carboxylic acid takes place.

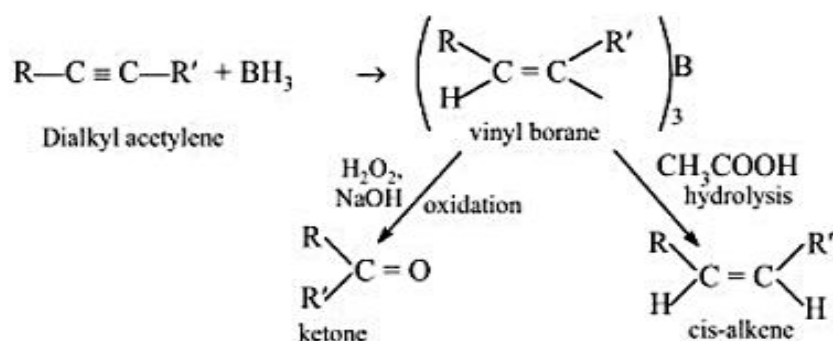


### Addition of Boron Hydride (Hydroboration) :

- (i) With mono-alkyl acetylene,  $\text{R}_2\text{BH}$  gives an intermediate which on hydrolysis gives alkene but on alkaline oxidation yields aldehyde.

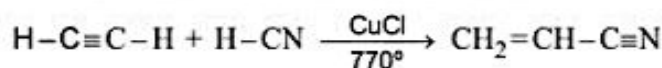


- (ii) With dialkyl acetylenes, the product of hydrolysis is cis-alkene and that of oxidation is a ketone.



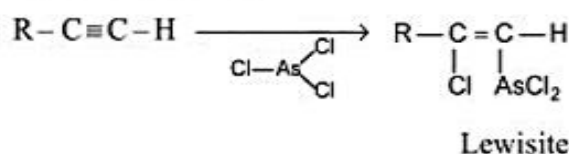
### Addition of HCN :

Addition takes place in the presence of CuCl



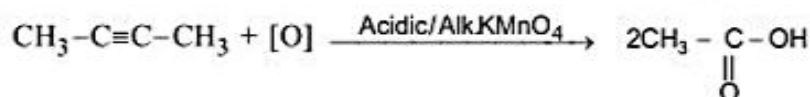
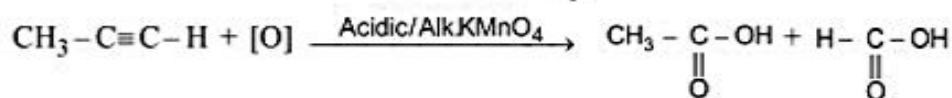
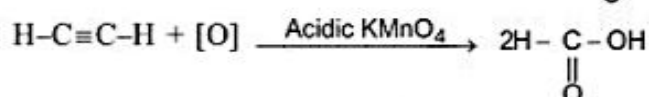
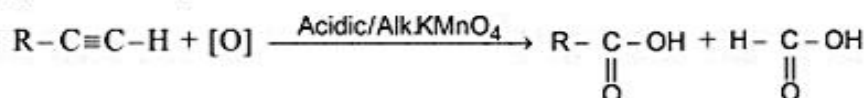
### Addition of AsCl<sub>3</sub> :

Lewisite is obtained

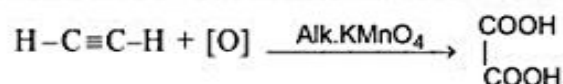


### Oxidation :

With acidic or alkaline KMnO<sub>4</sub> alkyne break into two parts from triply bonded carbon and every part forms respective acid.

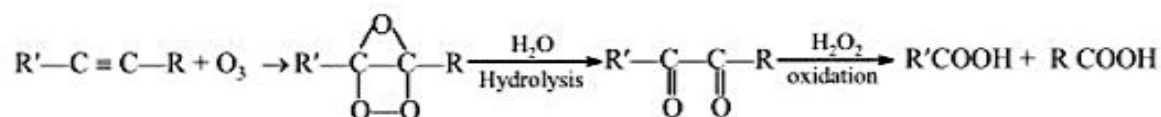


**Exception :** Acetylene forms oxalic acid with alkaline KMnO<sub>4</sub> exceptionally.



### Ozonolysis

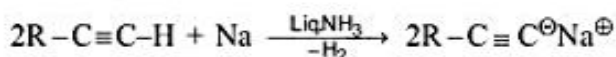
The ozonolysis of alkynes yields a mixture of carboxylic acids.



### Acidic nature of 1- Alkyne or Acetylene

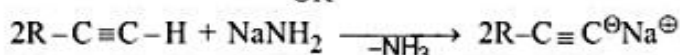
In 1- alkyne or acetylene, the H which is linked with sp hybridised carbon is called as acidic or active H. It can easily be substituted by metal or alkaline species. Hence 1- alkyne or acetylene are acidic in nature. eg.

#### Reaction with Na :



sodium alkynide

OR

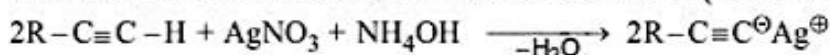


disodium acetylide

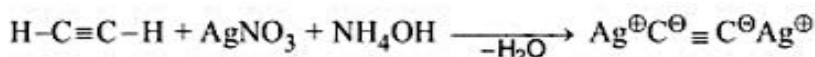
**Note :** Where this alkynide is treat with alkyl halide higher alkyne is obtained.



#### Reaction with Ammonical Silver Nitrate solution : (Tollen's Reagent)

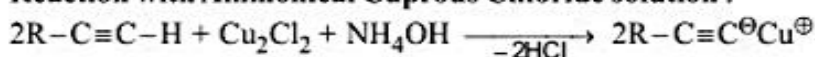


silver alkynide (white ppt)

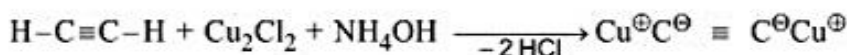


silver acetylide (white ppt)

#### Reaction with Ammonical Cuprous Chloride solution :



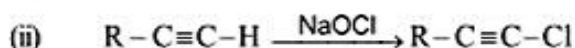
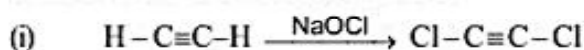
cuprous alkynide (red ppt.)



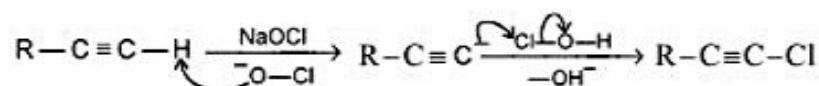
dicuprous acetylide (red ppt.)

#### Reaction with NaOCl :

Acidic hydrogen is substituted by 'Cl'



#### Mechanism :

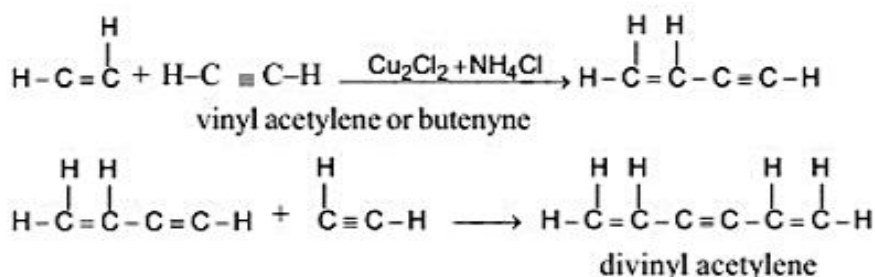


**Polymerisation Reactions :** Alkyne mainly shows addition polymerisation reactions.  
**Dimerisation and Cyclization**

**(a) Dimerisation :**

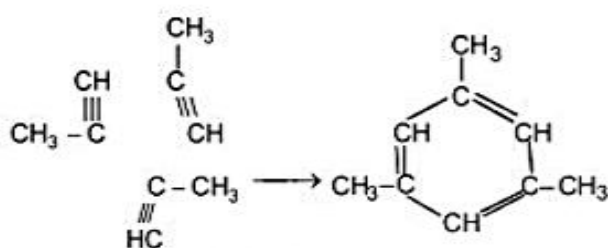
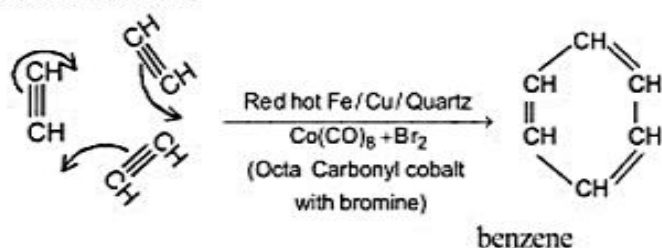
Two mole acetylene reacts with  $\text{Cu}_2\text{Cl}_2$  &  $\text{NH}_4\text{Cl}$  and forms vinyl acetylene.

**Note :** If acetylene would be in excess then product would be divinyl acetylene and the reaction is called *trimerisation*.



**(b) Trimerisation :**

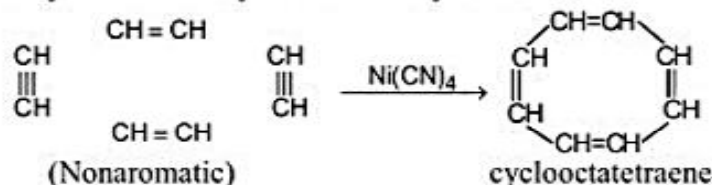
If three mole of acetylene is passed into red hot iron or Cu or quartz tube, then a cyclic trimer is formed which is called benzene.



mesitylene (having 3-1°, 3-2° & 3-3° carbons)

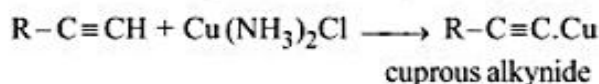
**Important :** Mesitylene can also be obtained from acetone by condensation polymerisation.

**(c) Tetramerisation :** According to the name four moles of acetylene are heated with nickel tetra cyanide, then acetylene forms a cyclic tetramer cyclo octa tetraene.



**Coupling:-**

**(a)** Alkyne form respective cuprous alkynide with ammonical cuprous chloride solution. When cuprous alkynide is reacted with potassium ferri cyanide [ $\text{K}_3\text{Fe(CN)}_6$ ] they converted into conjugated diyne.







- Q.6** When 2-butyne reacts with sodamide in an inert solvent in the presence of dilute HCl, the product formed is  
 (A) n-Butane (B) 2-Butene (C) 1-Butyne (D) 1-Propyne
- Q.7** Which of the following can not react with ammonical silver nitrate-  
 (A) Acetylene (B) Hexyne-1 (C) Phenyl acetaldehyde (D) hept-4-yne-2-ene
- Q.8** The hydrocarbon that reacts with ammonical cuprous chloride is-  
 (A) Essentially aromatic (B) Ethane (C) Ethyne (D) Ethene
- Q.9** The product of reaction  $\text{CH}_3\text{CH}_2\text{CH}_2\text{MgBr} + \text{HC} \equiv \text{CCH}_3 \rightarrow$  is  
 (A)  $\text{CH}_3\text{CH}_2\text{CH}_3$   
 (B)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{C} \equiv \text{CCH}_3$   
 (C)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$   
 (D)  $\text{CH}_3\text{CH}_2\text{CHO}$
- Q.10** 1-butyne can be distinguished from 2-butyne by using  
 (A) bromine water ( $\text{Br}_2$  in  $\text{CCl}_4$ )  
 (B) cold alk.  $\text{KMnO}_4$  (Baeyer's Reagent)  
 (C) ammoniacal solution of silver (Tollen's Reagent)  
 (D) diethyl ether
- Q.11** What is the chief product of reaction between  $\beta$ -butylene chloride and alc.  $\text{KOH}/\text{NaNH}_2$   
 (A) 1,2-butadiene (B) 1,3-butadiene (C) 2-butyne (D) 1-butyne
- Q.12** Chloroform is heated with Ag powder in laboratory what will be the product -  
 (A) Acetylene (B)  $\text{Ag}_2\text{O}$  (C)  $\text{CH}_2\text{Cl}_2$  (D)  $\text{CH}_4$
- Q.13** Ethylene dibromide on treating with alcoholic KOH gives -  
 (A)  $\text{C}_2\text{H}_6$  (B)  $\text{CH}_4$  (C)  $\text{C}_2\text{H}_4$  (D)  $\text{C}_2\text{H}_2$
- Q.14** Treatment of an alkyne with  $\text{H}_2$  in presence of palladised coke results in the formation of-  
 (A) Alkane (B) Alkane vigorously (C) Trans-alkene (D) cis-alkene

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#### ANSWER KEY

<b>Q.1</b>	A	<b>Q.2</b>	B	<b>Q.3</b>	D	<b>Q.4</b>	A
<b>Q.5</b>	A	<b>Q.6</b>	C	<b>Q.7</b>	D	<b>Q.8</b>	C
<b>Q.9</b>	A	<b>Q.10</b>	C	<b>Q.11</b>	C	<b>Q.12</b>	A
<b>Q.13</b>	D	<b>Q.14</b>	D				

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# REACTION CHART FOR ALKYNES

## GMP

- (1)  $\text{CH}_3\text{Br}-\text{CH}_2\text{Br} \xrightarrow{\text{alc. KOH or NaNH}_2}$
- (2)  $\text{CH}_3-\text{CHBr}_2 \xrightarrow{\text{alc. KOH, NaNH}_2}$
- (3)  $\text{CHCl}_3 \xrightarrow[\Delta]{\text{Ag powder}}$
- (4)  $\text{CHBr}_2-\text{CHBr}_2 \xrightarrow[\Delta]{\text{Zn dust}}$
- (5)  $\begin{array}{c} \text{CHBr} \\ || \\ \text{CHBr} \end{array} \xrightarrow{\text{Zn}}$
- (6)  $\text{CH}_2=\text{CH}-\text{Cl} \xrightarrow{\text{alc. KOH, NaNH}_2}$
- (7)  $\begin{array}{c} \text{HC}-\text{COONa} \\ || \\ \text{HC}-\text{COONa} \end{array} \xrightarrow{\text{Kolbe's electrolytic synthesis}}$
- (8)  $\text{CaC}_2 \xrightarrow{\text{H}_2\text{O}}$
- (9)  $2\text{C} + \text{H}_2 \xrightarrow[\text{Berthelot's process}]{\text{electric arc, } 1200^\circ\text{C}}$
- (10)  $\text{CH}_3-\text{C}\equiv\text{CH} \xrightarrow{\text{(i) Na (ii) R-X}}$
- (10)  $\text{CH}_3-\text{C}\equiv\text{CH} \xrightarrow{\text{(i) CH}_3\text{MgI (ii) R-X}}$



## GR

- (1)  $\xrightarrow[\text{Ni}]{\text{H}_2} \text{C}_2\text{H}_4, \text{C}_2\text{H}_6$
- (2)  $\xrightarrow{\text{X}_2} \text{C}_2\text{H}_2\text{X}_4$
- (3)  $\xrightarrow[\text{Peroxide}]{\text{HBr}} \text{CH}_3\text{BrCH}_2\text{Br}$
- (4)  $\xrightarrow[\text{No Peroxide}]{\text{HBr}} \text{CH}_3-\text{CHBr}_2$
- (5)  $\xrightarrow{\text{HOCl}} \text{Cl}_2\text{CHCHO}$
- (6)  $\xrightarrow{\text{HCN, Ba(CN)}_2} \text{CH}_2=\text{CHCN}$
- (7)  $\xrightarrow{\text{CH}_3\text{COOH, Hg}^{+2}} \text{CH}_3\text{CH(OCOCH}_3)_2$
- (8)  $\xrightarrow[\text{(Kucherov's reaction)}]{\text{Hg}^{+2}, 80^\circ\text{C, dil. H}_2\text{SO}_4} \text{CH}_3\text{CHO}$
- (9)  $\xrightarrow{\text{Conc. H}_2\text{SO}_4} \text{CH}_3\text{CH(HSO}_4)_2$
- (10)  $\xrightarrow{\text{AsCl}_3} \text{CHCl=CHAsCl}_2$
- (11)  $\xrightarrow[\text{HgSO}_4]{\text{C}_2\text{H}_5\text{OH/H}_2\text{O}} \text{CH}_3\text{CHO}$
- (12)  $\xrightarrow[\text{Ni(CO)}_4]{\text{CO+HOH}} \text{CH}_2=\text{CH-COOH}$
- (13)  $\xrightarrow[\text{Ni, } 160^\circ\text{C}]{\text{CO+EtOH}} \text{CH}_2=\text{CH-COOEt}$
- (14)  $\xrightarrow{\text{NaNH}_2} \text{NaC}\equiv\text{CNa}$
- (15)  $\xrightarrow[\text{(Tollen's Reagent)}]{\text{AgNO}_3 + \text{NH}_4\text{OH}} \text{AgC}\equiv\text{CAg}$
- (16)  $\xrightarrow{\text{Cu}_2\text{Cl}_2 + \text{NH}_4\text{OH}} \text{CuC}\equiv\text{CCu}$
- (17)  $\xrightarrow{\text{Combustion O}_2} \text{CO}_2 + \text{H}_2\text{O}$
- (18)  $\xrightarrow{\text{Bayer Reagent}} \begin{array}{c} \text{CHO} \\ | \\ \text{O} \\ | \quad | \\ \text{H}-\text{C}-\text{C}-\text{H} \\ | \quad | \\ \text{O} \quad \text{O} \end{array} \xrightarrow{+\text{H}_2\text{O}} \text{HCOOH}$
- (19)  $\xrightarrow{\text{O}_3} \begin{array}{c} \text{O} \\ | \quad | \\ \text{H}-\text{C}-\text{C}-\text{H} \\ | \quad | \\ \text{O} \quad \text{O} \end{array} \xrightarrow{+\text{H}_2\text{O}} \text{HCOOH}$
- (20)  $\xrightarrow[\text{(Red hot iron tube)}]{\text{Trimerisation}} \text{benzene}$
- (21)  $\xrightarrow[\text{[Ni(CN)}_2\text{]}]{\text{Trimerisation}} \text{C}_8\text{H}_8 \text{ or } 1,3,5,7\text{-cyclo octa tetraene}$
- (22)  $\xrightarrow[\text{[Cu(NH}_3)_2\text{]}^+]{\text{Dimerisation}} \text{butenyne}$
- (23)  $\xrightarrow[\Delta]{s} \begin{array}{c} \text{CH-CH} \\ || \quad || \\ \text{CH-CH} \\ \diagup \quad \diagdown \\ \text{S} \end{array}$
- (24)  $\xrightarrow[\text{(BF}_3\text{-HgO)}]{\text{CH}_3\text{OH}} \begin{array}{c} \text{CH(OCH}_3)_2 \\ | \\ \text{CH}_3 \end{array} \text{ methylal}$



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## PURIFICATION AND CHARACTERISATION OF ORGANIC COMPOUNDS

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### PURIFICATION OF ORGANIC COMPOUNDS

The methods to be employed depend on the physical state of the compound.

**Crystallisation :** This method is based on the differences in the solubility of the organic compound and its impurities in a solvent.

- (a) **Preparation of the solution :** Organic substance is powdered and is dissolved in a suitable solvent by heating. The amount of solvent should be just sufficient to dissolve the whole of the solid on heating.

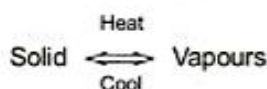
**Choice of Solvent.** The choice of solvent is very important in the crystallisation process. The main conditions of the solvent are:

- (i) The organic substance should dissolve in the solvent upon heating and it should get separated on cooling.
- (ii) The solvent should not dissolve the impurities.
- (iii) The solvent should not react chemically with the substance.

For example, suppose we want to purify sugar containing an impurity of common salt. This can be done by treating the mixture with ethanol around 350 K. The sugar will dissolve whereas common salt remains insoluble.

- (b) **Filtration of the solution.** The hot saturated solution is filtered preferably through a fluted filter paper placed in a glass funnel. The use of the fluted filter paper makes the filtration rapid. The jacket of the hot water funnel is heated from outside and this keeps the solution hot in the glass funnel. This will prevent the formation of crystals during filtration.
- (c) **Crystallisation.** The hot filtration is allowed to cool slowly and undisturbed in a beaker or in a crystallising dish. After some time the crystals of the pure compound are formed.
- (d) **Separation of the crystals.** The crystals formed are separated from the mother liquor by filtration. The filtration is normally done by use of Buckner funnel and a suction pump. This enables the filtration under reduced pressure and is therefore, quite fast.
- (e) **Drying of crystals.** The crystals are dried by pressing between the folds of filter paper and then placed in a stream of air oven for some time. The crystals are finally dried over sulphuric acid or calcium chloride in a desiccator.

**Sublimation :** Certain organic solids directly change from solid to vapour state on heating. This process is called sublimation. The vapours on cooling change back to the solid form





The sublimation process is used for the separation of those solids which sublime on heating from non-volatile solids. The process is generally used for the purification of camphor, naphthalene, anthracene, benzoic acid, etc. containing non-volatile impurities.

### **Distillation :**

This method is used for the purification of liquids which boil without decomposition and contain non-volatile impurities. The simple distillation involves its boiling point so that it is converted into vapours. On cooling the vapours, pure liquid is obtained.

The distillate contains pure liquid while the impurities are left behind in the distillation flask

e.g. Ether from ethyl alcohol.

### **Fractional Distillation :**

This process is used to separate a mixture of two or more miscible liquids which have boiling points close to each other. The fractionating column is a long tube provided with obstructions to the passage of the vapours moving upwards and liquid moving downwards. This method may be used to separate a mixture of acetone (b.p. 330K) and methyl alcohol (b.p. 338. K).

### **Distillation under Reduced pressure (Vaccum Distillation) :**

Certain liquids have a tendency to decompose at a temperature below their boiling points. Such liquids cannot be purified by ordinary distillation. Therefore vacuum distillation is used for liquids which decompose at a temperature below their normal boiling points.

Ex. glycerol boils with decomposition at 563K.

### **Steam distillation :**

The process of steam distillation is used for the separation and purification of liquid which is appreciably volatile in steam, from non-volatile components of a mixture. Thus, the process of steam distillations is used to purify the substances which

- (i) are volatile in steam but are not miscible with water
- (ii) possess sufficiently high vapour pressure at the boiling point temperature of water ( $100^{\circ}\text{C}$ )
- (iii) contain non-volatile impurities.

The process of steam distillation can be applied for the separation of a mixture of o-nitrophenol and p-nitrophenol. In this process, water vapours carry along with them vapours of o-nitrophenol which is more volatile and they get condensed in the receiver; p-nitrophenol with higher b.p. remains in the distillation flask. The method can also be used for the purification of impure sample of aniline.

### Chromatography :

This method is based on the differences in the rates at which the components of a mixture are adsorbed on a suitable adsorbent. There are many forms of chromatography such as column chromatography, paper chromatography, thin layer chromatography (TLC), gas chromatography, etc. The simplest method is column chromatography.

**Applications of chromatographic method.** This method has been used

- (i) To separate ortho and para nitro-anilines.
- (ii) To separate blue and red dyes.
- (iii) To separate and purify plant pigments and other natural products.

### Types of chromatography :

Based on the principle involved chromatography is classified into different categories. Two of these are.

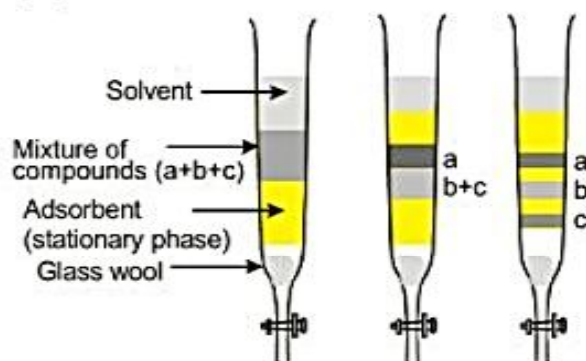
- (a) Adsorption chromatography, and
- (b) Partition chromatography

#### (a) Adsorption chromatography :

Adsorption chromatography is based on the fact that different compounds are adsorbed on an adsorbent to different degrees. Commonly used adsorbents are silica gel and alumina. When a mobile phase is allowed to move over a stationary phase (adsorbent), the components of the mixture move by varying distances over the stationary phase. Following are two main types of chromatographic techniques based on the principle of differential adsorption.

- (i) Column chromatography, and
- (ii) Thin layer chromatography.

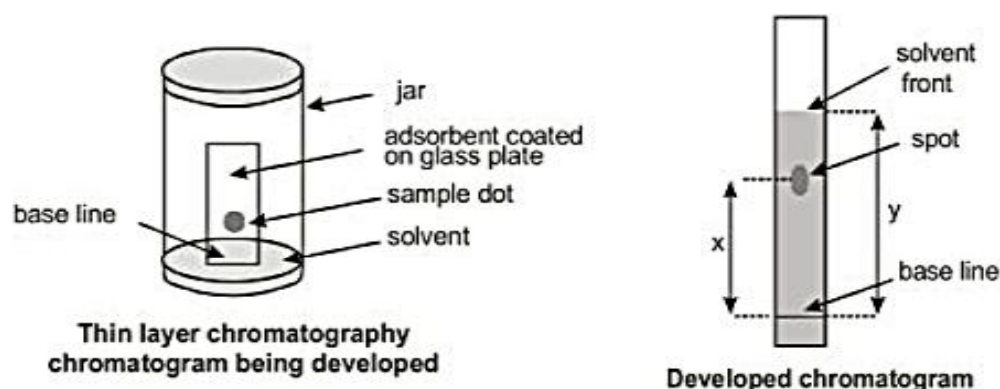
#### Column chromatography:



Column chromatography. Different stages of separation of components of a mixture

Column chromatography involves separation of a mixture over a column of adsorbent (stationary phase) packed in a glass tube. The column is fitted with a stopcock at its lower end. The mixture adsorbed on adsorbent is placed on the top of the adsorbent column packed in a glass tube. An appropriate eluant which is a liquid or a mixture of liquids is allowed to flow down the column slowly. Depending upon the degree to which the compounds are adsorbed, complete separation takes place. The most readily adsorbed substances are retained near the top and others come down to various distances in the column

#### Thin layer chromatography :



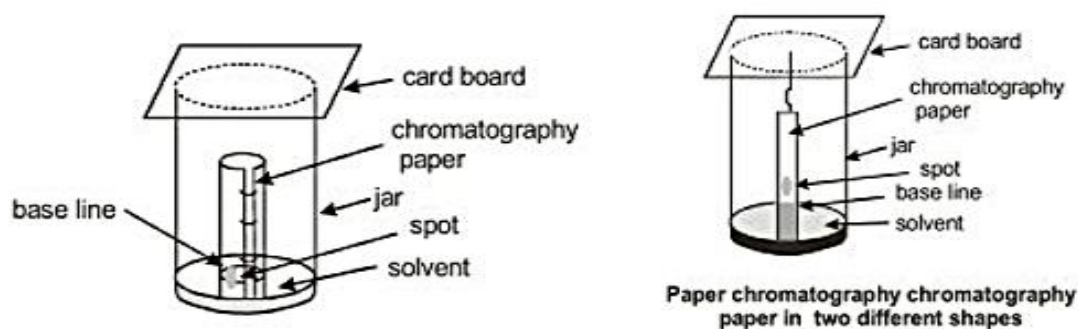
Thin layer chromatography (TLC) is another type of adsorption chromatography, which involves separation of substances of a mixture over a thin layer of an adsorbent coated on glass plate. A thin layer (about 0.2 mm thick) of an adsorbent (silica gel or alumina) is spread over a glass plate of suitable size. The plate is known as thin layer chromatography plate or chromaplate. The solution of the mixture to be separated is applied as a small spot about 2 cm above one end of TLC plate. The glass plate is then placed in a closed jar containing the eluant. As the eluant rises up the plate, the components of the mixture move up along with the eluant to different distances depending on their degree of adsorption and separation takes place. The relative adsorption of each component of the mixture is expressed in terms of its **retention factor** i.e.  $R_f$  value

$$R_f = \frac{\text{Distance moved by the substance from base line (x)}}{\text{Distance moved by the solvent from base line (y)}}$$

The spots of coloured compounds are visible on TLC plate due to their original colour. The spots of colourless compounds which are invisible to the eye but fluoresce, can be detected by putting the plate under ultraviolet light. Another detection technique is to place the plate in a covered jar containing a few crystals of iodine spots of compounds, which adsorb iodine will show up as brown spots. Sometimes an appropriate reagent may also be sprayed on the plate. For example, Amino acids may be detected by spraying the plate with ninhydrin solution



## (b) Partition Chromatography :



Partition chromatography is based on continuous differential partitioning of components of mixture between stationary and mobile phases. Paper chromatography is a type of partition chromatography. In paper chromatography, a special quality paper known as chromatography paper is used. Chromatography paper contains water trapped in it, which acts as the stationary phase.

A strip of chromatography paper spotted at the base with the solution of the mixture is suspended in a suitable solvent or a mixture of solvents. This solvent rises up the paper by capillary action and flows over the spot. The paper selectively retains different components according to their differing partition in the two phases. The paper strip so developed is known as a chromatogram. The spots of the separated coloured compounds are visible at different heights from the position of initial spot on the chromatogram. The spots of the separated colourless compounds may be observed either under ultraviolet light or by the use of an appropriate spray reagent as discussed under thin layer chromatography.

## QUALITATIVE ANALYSIS OF ORGANIC COMPOUNDS

The qualitative analysis of an organic compound involves the detection of all the elements present in it.

**Detection of Carbon and Hydrogen :** A small amount of the dry and powdered substance is mixed with about double the amount of pure and dry copper oxide. The mixture is heated in a well dried hard glass tube (fig) delivery tube is packed with glass wool containing anhydrous copper sulphate (white). When the mixture is heated, the carbon present in the compound is oxidised to carbon dioxide which turns lime water milky. The hydrogen present in the organic compound is oxidised to water which turns anhydrous copper sulphate in the bulb to blue.

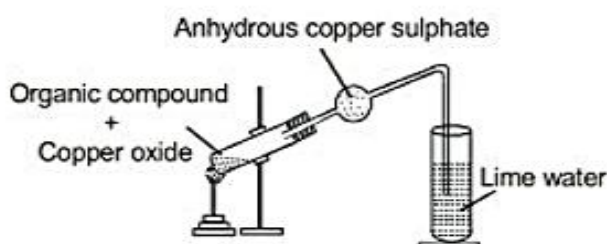
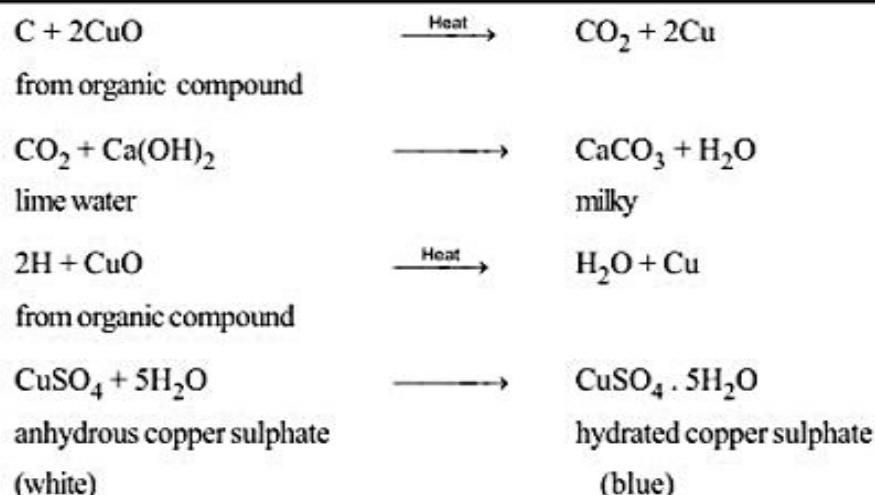


fig. Detection of carbon and hydrogen in an organic compound

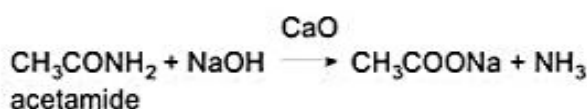




This method is known as copper oxide test.

**Detection of Nitrogen :** Nitrogen in an organic compound is detected by the following tests :

- (a) **Soda lime test.** A pinch of an organic compound is heated strongly with soda lime ( $NaOH + CaO$ ) in a test tube. If ammonia gas evolves, it indicates nitrogen.



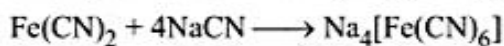
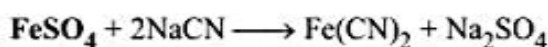
**Limitation :** This method has a limitation. A large number of organic compounds such as nitro and diazo compounds do not liberate ammonia on heating with sodalime.

- (b) **Lassaigne's method :** A small piece of a dry sodium metal is heated gently in a fusion tube till it melts to a shining globule. Then, a small amount of organic substance is added and the tube is heated strongly till it becomes red hot. The red hot tube is then cooled and filtered. The filtered liquid is known as sodium extract or Lassaigne's extract.

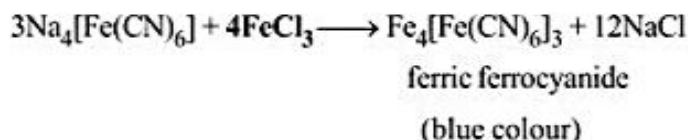
The Lassaigne's extract is usually alkaline. If not, it may be made alkaline by adding a few drops of a dilute solution of sodium hydroxide. A small amount of a freshly prepared ferrous sulphate solution is added to a part of sodium extract and the contents are warmed. A few drops of ferric chloride solution are then added to the contents and the resulting solution is acidified with dilute hydrochloric acid. The appearance of a bluish green or a blue colouration confirms the presence of nitrogen in the organic compound. The following chemical reactions occur during the test :



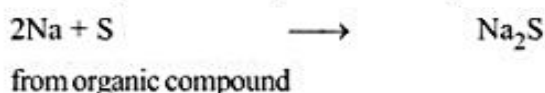
from organic  
compound



sodium ferrocyanide

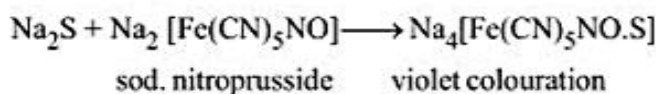


**Detection of Sulphur :** The sulphur in the compound reacts with sodium metal to form sodium sulphide.

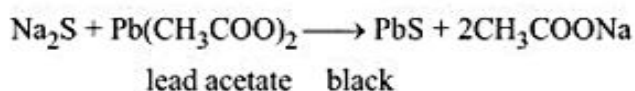


The Lassaigne's extract is divided into two parts and following tests are performed.

- (i) **Sodium nitroprusside test.** The one portion of the extract, a few drops of sodium nitroprusside are added. The appearance of violet colouration indicates sulphur.



- (ii) **Lead acetate test :** The other part of the Lassaigne's extract is acidified with acetic acid and then lead acetate solution is added. Formation of black precipitate confirms the presence of sulphur.



### Detection of Halogens :

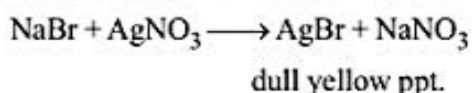
**Lassaigne's test.** Sodium extract is prepared as already. During fusion, sodium will combine with the halogen (from the organic compound) to form sodium halide



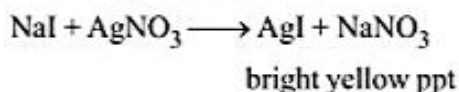
- (i) A white precipitate soluble in ammonium hydroxide solution indicates the presence of chlorine in the organic compound



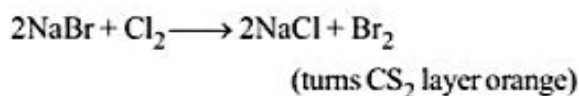
- (ii) A dull yellow precipitate partially soluble in ammonium hydroxide solution indicates the presence of bromine in the organic compound.

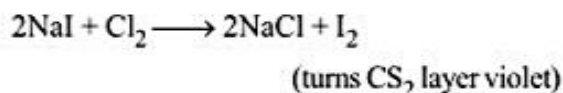


- (iii) A bright yellow precipitate, completely insoluble in ammonium hydroxide solution, indicates the presence of iodine in the organic compound.



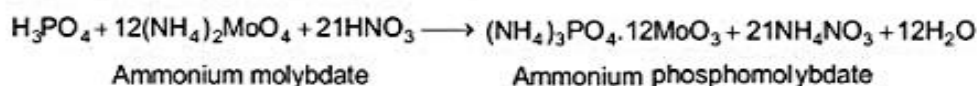
### Special test for bromine and iodine.





### Test of phosphorus :

The compound is heated with an oxidising agent (sodium peroxide). The phosphorus present in the compound is oxidised to phosphate. The solution is boiled with nitric acid and then treated with ammonium molybdate. A yellow colouration or precipitate indicates the presence of phosphorus.



## QUANTITATIVE ANALYSIS OF ORGANIC COMPOUNDS

### Estimation of Carbon and Hydrogen :

**Principle.** A known weight of the given dry organic compound is heated strongly with dry cupric oxide in an atmosphere of air or oxygen free from  $\text{CO}_2$ . The carbon and hydrogen of the organic compound are oxidised to  $\text{CO}_2$  and water vapour as :



(from compound)



(from compound)

#### Procedure :

Let the mass of organic compound taken =  $m$  g

Mass of water formed =  $m_1$  g

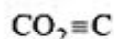
(increase in  $\text{CaCl}_2$  U-tube)

Mass of carbon dioxide formed =  $m_2$  g

(increase in potash tubes)

#### (a) Percentage of Carbon

We know that 1 mole of carbon dioxide (44 g) contains 1 gram atom of carbon (12g).



44 g of  $\text{CO}_2$  contain C = 12 g

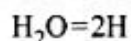
$m_2$  g of  $\text{CO}_2$  contains C =  $\frac{12}{44} \times m_2$  g

Hence Percentage of carbon =  $\frac{12m_2}{44 \times m} \times 100$



**(b) Percentage of Hydrogen**

We know that one mole of water (18g) contains 2 gram atom of hydrogen (2g)



18g of  $\text{H}_2\text{O}$  contain H = 2g

$$\therefore m_1 \text{ g of } \text{H}_2\text{O} \text{ contains H} = \frac{2}{18} \times m_1 \text{ g}$$

$$\text{Percentage of hydrogen} = \frac{2m_1}{18 \times m} \times 100$$

$$\text{Percentage of C} = \frac{12}{44} \times \frac{\text{Mass of CO}_2 \text{ formed}}{\text{Mass of compound taken}} \times 100$$

$$\text{Percentage of H} = \frac{2}{18} \times \frac{\text{Mass of H}_2\text{O formed}}{\text{Mass of compound taken}} \times 100$$

**Estimation of Nitrogen :**

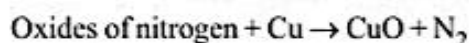
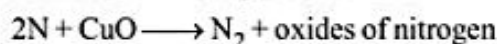
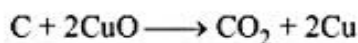
There are two methods for the estimation of nitrogen

(i) Duma's method

(ii) Kjeldahl's method

**Duma's method :**

**Principle of the method.** A known mass of an organic compound is heated with dry cupric oxide in an atmosphere of carbon dioxide. The carbon and hydrogen are oxidised to carbon dioxide and water respectively while nitrogen is set free. If any oxide of nitrogen is produced during this process, it is reduced to nitrogen by passing over a heated copper gauze. The gaseous mixture is collected over an aqueous solution of KOH when all the gases except nitrogen are absorbed. The volume of nitrogen produced is measured at room temperature and atmospheric pressure. From the volume of  $\text{N}_2$  produced, percentage of nitrogen in the sample can be calculated.



Let the mass of organic compound =  $w$  g

The volume of nitrogen collected =  $V \text{ cm}^3$

Atmospheric pressure (from barometer) =  $P$  mm of Hg

Room temperature =  $t^\circ\text{C}$

Aqueous tension at  $t^\circ\text{C}$  =  $a$  mm of Hg

Pressure of dry nitrogen =  $(P - a)$  mm of Hg

Let us first convert the volume of nitrogen to volume at S.T.P.



Experimental conditions S.T.P. conditions

$$P_1 = (P - a) \text{ mm Hg}$$

$$P_2 = 760 \text{ mm}$$

$$T_1 = (273 + t) \text{ K}$$

$$T_2 = 273$$

$$V_1 = V \text{ cm}^3$$

$$V_2 = ?$$

Applying gas equation  $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$

$$\therefore V_2 = \frac{P_1 V_1 T_2}{P_2 T_1} = \frac{(P - a) \times V \times 273}{760 (273 + t)} = x \text{ cm}^3 \text{ (say)}$$

Now  $22400 \text{ cm}^3$  of  $\text{N}_2$  at S.T.P. weight = 28 g

$$x \text{ cm}^3 \text{ of } \text{N}_2 \text{ at S.T.P. will weigh} = \frac{28}{22400} \times x \text{ g}$$

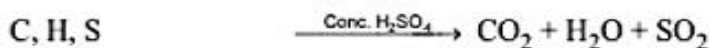
$$\therefore \text{Percentage of nitrogen} = \frac{\text{Mass of nitrogen}}{\text{Mass of organic compound}} \times 100$$

$$= \frac{28x \times 100}{22400 \times w}$$

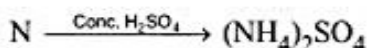
**Kjeldahl's method :** This method cannot be used for

- (i) Organic compounds containing nitrogen in the ring such as pyridine, quinoline, etc.
- (ii) Organic compounds containing nitrogen ( $-\text{NO}_2$ ) and diazo ( $-\text{N}=\text{N}-$ ) groups.

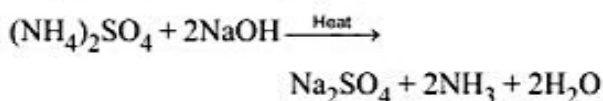
**Principle :** A known weight of the organic compound is heated with conc.  $\text{H}_2\text{SO}_4$  so that nitrogen is quantitatively converted into ammonium sulphate. The solution is then heated with excess of sodium hydroxide. The ammonia gas evolved is passed into a known but excess volume of standard acid ( $\text{HCl}$  or  $\text{H}_2\text{SO}_4$ ). The acid left unused is estimated by titrating the solution with standard alkali. From the amount of acid left unused the amount of acid used for neutralisation of ammonia can be calculated. From this percentage of nitrogen can be calculated.

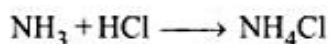
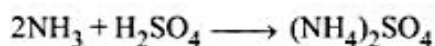


(from organic compound)



(from organic compound)      ammonium sulphate





### Calculations

Let the mass of organic compound =  $w$  g

Volume of standard acid taken =  $V \text{ cm}^3$

Normality of acid =  $N_1$

Let vol. of standard alkali used for neutralisation of unused acid =  $V_2 \text{ cm}^3$

Normality of standard alkali =  $N_2$

$$\underbrace{N_1 V_1}_{\text{alkali}} = \underbrace{N_2 V_2}_{\text{acid}}$$

Let this volume of  $v \text{ cm}^3$

$\therefore$  Vol. of acid used for neutralisation of ammonia

$$= (V - v) \text{ cm}^3 \text{ of } N_1 \text{ normality}$$

$\therefore$  Ammonia liberated =  $(V - v) \text{ cm}^3$  of  $N_1$  solution

Now,  $1000 \text{ cm}^3$  of  $1N \text{ NH}_3$  solution contains nitrogen =  $14 \text{ g}$

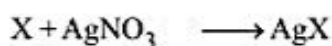
$$(V - v) \text{ cm}^3 \text{ of } N_1 \text{ NH}_3 \text{ solution contains nitrogen} = \frac{14(V - v) \times N_1}{1000} \text{ g}$$

$$\begin{aligned} \text{Percentage of nitrogen} &= \frac{\text{Mass of nitrogen}}{\text{Mass of organic compound}} \times 100 = \frac{14(V - v) \times N_1}{1000} \times \frac{100}{w} \\ &= \frac{1.4(V - v) \times N_1}{w} \end{aligned}$$

### Estimation of Halogens :

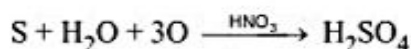
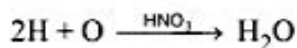
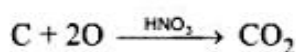
#### Carius method :

**Principle :** A known mass of the organic substance is heated with fuming  $\text{HNO}_3$  in a Carius tube. The silver halide so obtained is separated, washed, dried and weighed. From the weight of silver halide formed, the percentage of halogen can be calculated.



Halogen

Carbon, hydrogen or sulphur present in the compound will be oxidised to  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and  $\text{H}_2\text{SO}_4$  respectively.



**Calculations :**

Let the mass of organic compound be  $w$  g

Mass of silver halide formed =  $a$  g

Now,  $\text{AgX} = \text{X}$

$108 + \text{X}$  parts by weight of silver halide contains  $\text{X}$  parts by weight of halogen ( $\text{X}$  is its atomic mass)

$(108 + \text{X})$  g of silver halide give halogen =  $\text{X}$

$a$  g of silver halide will give halogen =  $\frac{\text{X}}{(108 + \text{X})} \times a$  g

$$\therefore \text{Percentage of halogen} = \frac{\text{Mass of halogen}}{\text{Mass of organic compound}} \times 100 = \frac{\text{X} \times a}{(108 + \text{X})} \times \frac{100}{w}$$

Here  $\text{X}$  is the atomic mass of halogen, e.g.

$\text{Cl} = 35.5$ ,  $\text{Br} = 80$  (79.9 exact),

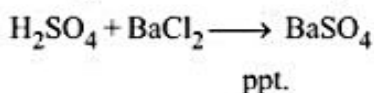
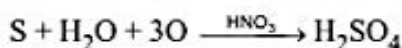
$\text{I} = 127$  (126.9 exact)

$$\text{Percentage of halogen} = \frac{\text{Atomic mass of halogen} \times \text{Mass of silver halide}}{(108 + \text{At. mass of halogen}) \times \text{Mass of organic substance}} \times 100$$

**Estimation of Sulphur**

Sulphur is estimated by Carius method.

**Principle :** A known mass of the organic compound is heated with fuming  $\text{HNO}_3$  in a sealed tube when sulphur is quantitatively converted into sulphuric acid. It is then precipitated with barium chloride as barium sulphate. The precipitate is filtered, washed, dried and weighed. From the weight of  $\text{BaSO}_4$  formed, the percentage of sulphur can be calculated. The main reactions are :

**Calculations :**

Let the mass of organic compound =  $w$  g

Mass of  $\text{BaSO}_4$  formed =  $a$  g

$\text{BaSO}_4 \equiv \text{S}$

$$\begin{aligned} 137 + 32 + 64 &= 32 \\ &= 233 \end{aligned}$$

233 g of  $\text{BaSO}_4$  contain sulphur = 32 g

$a$  g of  $\text{BaSO}_4$  will contain sulphur =  $\frac{32 \times a}{233}$  g

$$\text{Percentage of sulphur} = \frac{\text{Mass of sulphur}}{\text{Mass of organic compound}} \times 100 = \frac{32a}{233} \times \frac{100}{w}$$

## SOLVED EXAMPLES

**Q.1** In Lassaigne's test when both N and S are present, blood red colour obtained is due to the formation of-

- (A) Ferric ferrocyanide (B) Ferric sulphocyanide  
(C) Ferric cyanide (D) None

**Ans.** (B)

**Sol.**  $3 \text{ NaCNS} + \text{FeCl}_3 \longrightarrow \text{Fe(CNS)}_3 + 3\text{NaCl}$   
(Red)

**Q.2** On complete combustion, 0.246g of an organic compound gave 0.198g of carbon dioxide and 0.1014g of water. Determine the percentage composition of carbon and hydrogen in the compound.

**Sol.** Percentage of carbon =  $\frac{12 \times 0.198 \times 100}{44 \times 0.246} = 21.95 \%$

Percentage of hydrogen =  $\frac{2 \times 0.1014 \times 100}{18 \times 0.246} = 4.58 \%$

**Q.3** In duma's method for estimation of nitrogen., 0.3g of an organic compound gave 50mL of nitrogen collected at 300K temperature and 715 mm pressure. Calculate the percentage composition of nitrogen in the compound. (Aqueous tension at 300K = 15 mm)

**Sol.** Volume of nitrogen collected at 300K and 715 mm pressure is 50mL

Actual pressure = 715-15 = 700 mm

Volume of nitrogen at STP =  $\frac{273 \times 700 \times 50}{300 \times 760} = 41.9 \text{ mL}$

22,400 mL of  $\text{N}_2$  at STP weight = 28g

41.9 mL of nitrogen weights =  $\frac{28 \times 41.9}{22400} \text{ g}$

Percentage of nitrogen =  $\frac{28 \times 41.9 \times 100}{22400 \times 0.3} = 17.46\%$

**Q.4** During estimation of nitrogen present in an organic compound by Kjeldahl's method, the ammonia evolved from 0.5 g of the compound in Kjeldahl's estimation of nitrogen, neutralized 10 mL of 1 M  $\text{H}_2\text{SO}_4$ . Find out the percentage of nitrogen in the compound.

**Sol.** 1 M of 10 mL  $\text{H}_2\text{SO}_4$  = 1M of 20mL  $\text{NH}_3$  1000 mL of 1M ammonia contains 14 g nitrogen

20 mL of 1M ammonia contains  $\frac{14 \times 20}{1000} \text{ g}$  nitrogen

Percentage of nitrogen =  $\frac{14 \times 20 \times 100}{1000 \times 0.5} = 56.0 \%$

**Q.5** In Carius method of estimation of halogen, 0.15 g of an organic compound gave 0.12 g of AgBr. Find out the percentage of bromine in the compound.



**Sol.** Molar mass of AgBr =  $108 + 80 = 188 \text{ g mol}^{-1}$

188 g AgBr contains 80 g bromine

0.12 g AgBr contains  $\frac{80 \times 0.12}{188}$  g bromine

Percentage of bromine =  $\frac{80 \times 0.12 \times 100}{188 \times 0.15} = 34.04 \%$

**Q.6** In sulphur estimation, 0.157 g of an organic compound gave 0.4813 g of barium sulphate. What is the percentage of sulphur in the compound?

**Sol.** Molecular mass of  $\text{BaSO}_4 = 137 + 32 + 64$   
 $= 233 \text{ g}$

233 g  $\text{BaSO}_4$  contains 32 g sulphur

0.4813 g  $\text{BaSO}_4$  contains  $\frac{32 \times 0.4813}{233}$  g sulphur

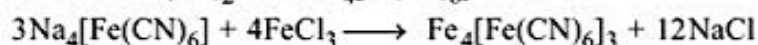
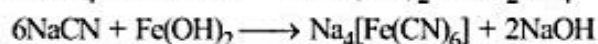
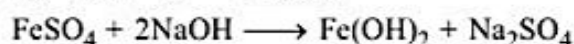
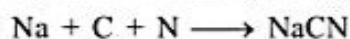
Percentage of sulphur =  $\frac{32 \times 0.4813 \times 100}{233 \times 0.157} = 42.10 \%$

**Q.7** In Lassaigne's test for nitrogen, the blue colour is due to the formation of-

- (A) Ferric ferrocyanide
- (B) Potassium ferrocyanide
- (C) Sodium ferrocyanide
- (D) Sodium cyanide

**Ans.** (A)

**Sol.** In Lassaigne's test substance is heated strongly with sodium metal then water extract is boiled with alkaline  $\text{FeSO}_4$  solution and after cooling  $\text{FeCl}_3$  solution and excess of HCl is added in it. If prussian blue or green ppt. is obtained then Nitrogen is confirmed-



sodium ferrocyanide

prussian blue or green

(ferric ferrocyanide)

**Q.8** In sodium fusion test of organic compounds, the nitrogen of an organic compound is converted to-

- (A) Sodamide
- (B) Sodium cyanide
- (C) Sodium nitrite
- (D) Sodium nitrate

**Ans.** (B)

**Sol.**  $\text{Na} + \text{C} + \text{N} \xrightarrow{\text{fusion}} \text{NaCN}$

**Q.9** A compound which does not give a positive test in the Lassaigne's test for 'N' is-

- (A) Glycine
- (B) Phenyl hydrazine
- (C) Urea
- (D) Azobenzene

**Ans.** (D)

**Sol.** Azobenzene does not give positive test in Lassaigne's test for N.

**Q.10** Liebig method is used for the estimation of-

- (A) Nitrogen (B) Sulphur  
(C) Carbon and Hydrogen (D) Halogens

**Ans.** (C)

**Sol.** Liebig method is used for the estimation of carbon and hydrogen.

**Q.11** The quantitative determination of halogen in an organic compound is known as-

- (A) Dumas method (B) Carius method (C) Kjeldahl method (D) Leibig method

**Ans.** (B)

**Sol.** The quantitative determination of halogen in an organic compound is called as carius method.

**Q.12** 0.2475g of an organic compound gave on combustion 0.4950g of carbon dioxide and 0.2025 g of water. The percentage of carbon and hydrogen are-

- (A) 54.54, 9.09 (B) 52.54, 8.09 (C) 120, 5.8 (D) None

**Ans.** (A)

**Sol.** Wt. of organic compound = 0.2475 g

Wt. of  $\text{CO}_2$  produced = 0.4950 g

Wt. of  $\text{H}_2\text{O}$  produced = 0.2025 g

Percentage of carbon

$$= \frac{12}{44} \times \frac{\text{Wt. of } \text{CO}_2}{\text{Wt. of compound}} \times 100$$

$$= \frac{12}{44} \times \frac{0.4950}{0.2475} \times 100 = 54.54$$

Percentage of hydrogen

$$= \frac{2}{18} \times \frac{\text{Wt. of } \text{H}_2\text{O}}{\text{Wt. of compound}} \times 100$$

$$= \frac{2}{18} \times \frac{0.2025}{0.2475} \times 100 = 9.09$$

**Q.13** 0.257 g of an organic substance was heated with conc  $\text{H}_2\text{SO}_4$  and then distilled with excess of strong alkali. The ammonia gas evolved was absorbed in 50 ml of N/10 HCl which required 23.2 ml of N/10 NaOH for neutralisation at the end of the process. The percentage of nitrogen in the compound is-

- (A) 14.6 (B) 18.0 (C) 17.0 (D) 15.5

**Ans.** (A)

**Sol.** Volume of  $\frac{\text{N}}{10}$  HCl taken = 50ml

Volume of  $\frac{\text{N}}{10}$  NaOH used for neutralisation of unused acid = 23.2 ml

Now  $N_1 V_1(\text{NaOH}) = N_2 V_2(\text{HCl})$

23.2 ml of  $\frac{\text{N}}{10}$  NaOH  $\equiv$  23.2 ml of  $\frac{\text{N}}{10}$  HCl

$\therefore$  Volume of  $\frac{N}{10}$  HCl unused = 23.2 ml

$\therefore$  Volume of  $N/10$  HCl required for neutralization of  $NH_3$  = 50 - 23.2 = 26.8 ml

26.8 ml of  $\frac{N}{10}$  HCl = 26.8 ml of  $N/10$   $NH_3$

1000 ml of 1N  $NH_3$  solution contains nitrogen = 14 g

26.8 ml of  $NH_3$  solution contains nitrogen =  $\frac{14 \times 26.8}{10 \times 1000}$

Percentage of nitrogen =  $\frac{14 \times 26.8 \times 100}{10 \times 1000 \times 0.257} = 14.6\%$

**Q.14** 0.395 g of an organic compound by Carius method for the estimation of sulphur gave 0.582 g of  $BaSO_4$ . The percentage of sulphur in the compound is-

- (A) 20.24                      (B) 35                      (C) 40                      (D) 45

**Ans.** (A)

**Sol.** Mass  $BaSO_4$  = 0.582 g

We know  $BaSO_4 \equiv S$   
                   233                      32

233 g of  $BaSO_4$  contain sulphur = 32 g

0.582 g of  $BaSO_4$  contains sulphur =  $\frac{32}{233} \times 0.582$

Percentage of sulphur

$$= \frac{\text{Wt. of sulphur}}{\text{Wt. of compound}} \times 100 = \frac{32 \times 0.582}{233 \times 0.395} \times 100 = 20.24 \%$$

**Q.15** Liquid which decompose below their normal boiling points can be distilled at lower temperature by-

- (A) Increasing the pressure                      (B) Decreasing the pressure  
 (C) Heating in water bath                      (D) Heating in sand bath

**Ans.** (B)

**Sol.** B.pt. gets lowered at low pressure.

**Q.16** A bottle containing two immiscible liquids is given to you. They may be separated by using-

- (A) Fractionating column                      (B) Separating funnel  
 (C) Vacuum distillation                      (D) Steam distillation

**Ans.** (B)

**Sol.** Being immiscible liquids, they form different layers.



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## ENVIRONMENTAL CHEMISTRY

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### INTRODUCTION

- (i) Pollution may be defined as any undesirable change in the physical, chemical or biological characteristics of air, water and soil which may cause any harm to man and other living organisms of the environment.

#### Types of pollutants

The agents causing pollution are termed as **pollutants**.

On the basis of form of their occurrence, pollutants are divided into two categories.

- (i) **Primary pollutants** – These are present in the same form in which they are produced. eg. carbon monoxide, DDT
- (ii) **Secondary pollutants** – These are formed by reaction between the primary pollutants in the presence of sunlight eg. PAN, Ozone,  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$  etc. Nitrogen oxides and hydrocarbons react photochemically to produce peroxyacetyl nitrates (PAN) and ozone.  
The secondary pollutants may be more toxic than the primary ones. The phenomenon is called **synergism**.

On the basis of their degradation, pollutants are divided into two categories.

- (i) **Biodegradable Pollutants** – Pollutants which are decomposed or degraded by biological or microbial action are called biodegradable pollutants eg. domestic sewage.
- (ii) **Non-biodegradable Pollutants** – Pollutants which are not decomposed or degraded by living organisms or micro organisms are called non-biodegradable pollutants eg. DDT, glass, plastics, aluminium cans, phenolic compounds, pesticides, radioactive substances, heavy metals like mercury, lead, cadmium etc.

On the basis of their existence in nature, pollutants are divided into two categories.

- (i) **Quantitative pollutants** – These are naturally present in nature and are also added by man. These become pollutants only when their concentration reaches beyond a threshold value in the environment. eg.  $\text{CO}_2$ .
- (ii) **Qualitative pollutants** – These are not present in nature but are added in nature only due to human activities eg. insecticides, fungicides, herbicides etc.

### KINDS OF POLLUTION

On the basis of environmental study pollution is of following types.

**Air pollution**

**Water pollution**

**Soil pollution**

**Noise pollution**

**Radioactive pollution**

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**Air pollution –**

- (i) It is mainly caused by industries and automobiles. Automobiles are the greatest polluter of the atmosphere and are responsible for 75% of noise pollution and about 60-80% of air pollution of big cities.
- (ii) The combustion of fossil fuels (coal, oil, gas etc.) releases CO, CO<sub>2</sub>, nitrogen oxides, fluorides, hydrocarbons etc. into atmosphere usually in the form of smoke causing air pollution.
- (iii) Particulate matters released by mills, factories and mines also cause air pollution.
- (iv) Some of the natural air pollutants are pollen grains, spores, volcanoes etc.

**MAJOR AIR POLLUTANTS****Carbon monoxide –**

- (i) It is formed by incomplete combustion of fuels in various industries, automobiles etc.
- (ii) CO accounts for about 50% of total air pollution. It is largest pollutant in Delhi's air.
- (iii) CO combines with haemoglobin, produces **carboxyhaemoglobin** and therefore decreases oxygen carrying capacity leading to hypoxia, headache, decreased vision, muscular weakness, nausea, exhaustion etc.
- (iv) When 50% of haemoglobin has been transformed into carboxyhaemoglobin, then death occurs due to CO-poisoning leading to anoxia (oxygen starvation)

**Carbon dioxide –**

- (i) It is a **green house gas**. It is produced due to combustion of fuels, volcanic eruptions and during the process of respiration.
- (ii) Its average concentration in the atmosphere is 300 ppm (0.03%) .
- (iii) It is normally not an atmospheric pollutant, but under very high concentration it may act as a pollutant.
- (iv) It causes **Global warming** .

**Sulphur dioxide (SO<sub>2</sub>) –**

- (i) It is produced during combustion of fossil fuels (mainly coal) and smelting of sulphur containing ores.
- (ii) It causes acid rain (gaseous SO<sub>2</sub> oxidises to SO<sub>3</sub>, which on combination with water forms H<sub>2</sub>SO<sub>4</sub>).
- (iii) Acid rain is 60-70% due to SO<sub>2</sub> and SO<sub>3</sub>, and 30-40% due to NO<sub>2</sub> and NO<sub>3</sub>.
- (iv) Due to acid rain the leaves develop chlorotic and necrotic spots.
- (v) SO<sub>2</sub> corrodes stones, metals, leather, paper and fabrics. There is deterioration of colour and lustre of fabrics, stones and painted surfaces.

**Hydrocarbons –**

- (i) They are produced naturally (e.g. marsh gas CH<sub>4</sub>) and by burning of petroleum.
  - (ii) Benzene (C<sub>6</sub>H<sub>6</sub>) is a major constituent of petrol and automobile exhaust.
  - (iii) Hydrocarbons are carcinogenic, cause irritation of eyes and mucous membrane.
  - (iv) Benzene is a known carcinogen causing **leukemia**.
-

- (v) Ethylene ( $C_2H_4$ ) causes premature senescence and abscission in many plants especially in orchids and cotton,
- (vi) Methane (marsh gas) has the potential of destroy ozone.

#### **Nitrogen oxides –**

- (i) There are three oxides of nitrogen which act as air pollutants : Nitric oxide (NO), nitrogen dioxide ( $NO_2$ ) and nitrogen trioxide.
- (ii) Nitrogen and oxygen combine together at high temperature in any combustion process to produce nitrogen oxides.
- (iii) These are also released by furnaces, forest fires, industries and denitrifying bacteria.
- (iv) NO is less toxic but  $NO_2$  is a poisonous gas.
- (v) Nitrogen oxides are responsible for forming photochemical smog.

#### **Fluorides –**

- (i) Fluorides are emitted during refinement of aluminium and rock phosphates .
- (ii) Fluorides cause necrosis and chlorosis of leaf tips and leaf margins.
- (iii) In human fluorides cause mottling of teeth, weak bones, boat-shaped posture, knocking knees etc.
- (iv) Disease caused by fluoride is known as **fluorosis**.

#### **Particulate matter –**

- (i) It is the non-gaseous matter in the atmosphere.
- (ii) It consists of soot, dust, mist, fibres, fly ash, fur, spores, pollen grains etc.
- (iii) It is of two types settleable (larger than  $10\ \mu m$ ) and suspended (less than  $10\ \mu m$ )
- (iv) SPM (suspended particulate matter) is classified into 3 categories –
  - (a) Aerosols (less than  $1\ \mu m$ )
  - (b) Dust (solid particles with more than  $1\ \mu m$  diameter)
  - (c) Mist (liquid particles with more than  $1\ \mu m$  diameter)
- (v) It is added in the atmosphere by burning of fuels.

#### **Aerosols –**

- (i) These are chemicals released in the air with force in the form of mist or vapour by jet planes.
- (ii) Aerosols contain **CFC (chlorofluorocarbons)** which destroy ozone layer in the stratosphere. This permitting some more harmful
- (iii) U.V. radiations to reach the earth surface, U.V. radiations cause skin cancer and increases mutation rates.
- (iv) Ozone acts as preventive shield against the U.V. rays.
- (v) Freons are several CFMS (chlorofluoromethanes) released into troposphere where they dissociates and release free chlorine that causes depletion of ozone.
- (vi) Freon or CFC also used in refrigerator, air conditioners and in making plastic foams.

#### **Effect of air pollutants –** Air pollutants are involved in causing four major environmental effects :

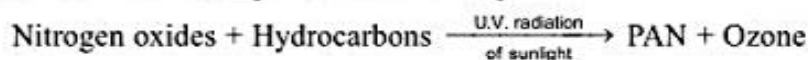
- |                          |                             |
|--------------------------|-----------------------------|
| (i) Smog                 | (ii) acid rain              |
| (iii) global warming and | (iv) ozone layer depletion. |



**Smog –**

- (i) The term smog was coined by Des Voeux.
- (ii) It is produced by the combination of smoke and fog.
- (iii) It causes silvering/glazing and necrosis in plants, allergies and asthma/bronchitis in human.
- (iv) Smog is of two types :
  - (a) **Classical or London smog or sulphurous smog** – It occurs at low temperature and contains  $\text{H}_2\text{S}$ ,  $\text{SO}_2$ , smoke and dust particles. It was first observed in winter months at London in 1905. It is formed due to domestic and industrial combustion of coal.
  - (b) **Photochemical smog or Los Angeles smog** – It was first observed in the mid day at Los Angeles in 1943. The cause of this smog was thought to be due to combustion of petroleum in automobiles.

Photo chemical smog occurs at high temperature over cities and towns. It is formed by the reaction of two air pollutants nitrogen oxides (mainly  $\text{NO}_2$ ) and hydrocarbons (HC) that react with one another in the presence of UV radiations of sunlight to produce ozone ( $\text{O}_3$ ) and PAN (peroxy acetyl nitrate) which constitute the photochemical smog.



Ozone and PAN are commonly referred to as oxidants.

Breathing ozone affects the respiratory and nervous system, resulting in headache, respiratory distress and exhaustion. It also causes irritation in eyes and asthma. The ozone is known to destroy crops of potato, alfalfa and spinach to the extent of 50%. It also damages leaves of tobacco, tomato and pine as also the grape fruits. Besides, the PAN also blocks Hill reaction of photosynthesis.

**Acid rain –**

- (i) The coal and oil burned by power plants release  $\text{SO}_2$  into the air.
- (ii) Automobile exhaust puts  $\text{NO}_2$  in the air.
- (iii) Both  $\text{SO}_2$  and  $\text{NO}_2$  are converted to acids ( $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  respectively) when they combine with water vapour in the presence of  $\text{O}_2$  in the atmosphere. These acids return to the earth as acid rain.
  - (A)
 

$\text{NO} + \text{O}_3$	$\longrightarrow$	$\text{NO}_2 + \text{O}_2$
$\text{NO}_2 + \text{O}_3$	$\longrightarrow$	$\text{NO}_3 + \text{O}_2$
$\text{NO}_2 + \text{NO}_3$	$\longrightarrow$	$\text{N}_2\text{O}_5$
$\text{N}_2\text{O}_5 + \text{H}_2\text{O}$	$\longrightarrow$	$2\text{HNO}_3$
  - (B)  $2\text{SO}_2 + \text{O}_2 \xrightarrow{\text{No. Soot or Metal ions}} 2\text{SO}_3$
- (iv) The pure rain has a pH of about 5.6 while the acid rain has pH below 5.6.
- (v) Acid rain is actually a mixture of  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  ( usually 60-70%  $\text{H}_2\text{SO}_4$  and 30-40%  $\text{HNO}_3$  )
- (vi) Acid rain affects the ability of the trees to tolerate cold temperatures and the weakened trees are killed by cold conditions or become more susceptible to diseases.
- (vii) Acid rain leaches lead, mercury and calcium, from the soils and rocks and discharges them into rivers and lakes. The metals may become concentrated in fish and then passed on to people through food chain.
- (viii) Acid rain also damages building materials, including steel, paint, plastics, cement and marble.

### Green house effect and Global warming –

- (i) The sunlight that reaches to the earth, warms both atmosphere and the earth surface. The earth's atmospheric system then radiates the heat as infra-red radiations.
- (ii) Gases like  $\text{CO}_2$ ,  $\text{CH}_4$ , CFCs,  $\text{NO}_2$  are strong absorbers of long-wave or infra-red radiations emitted by the surface of the earth, and warm the earth's atmosphere. This is called the **green house effect** because it is like the glass panel of a green house that allows sunlight to pass through and then traps the resulting heat inside the structure.
- (iii)  $\text{CO}_2$  is the principal green house gas responsible for warming of the earth.
- (iv)  $\text{CO}_2$  is rising into the atmosphere slowly as a result of large scale burning of fossil fuels (coal, oil etc), volcanic activities and respiration
- (v) 50% of the increase in earth's temperature is due to  $\text{CO}_2$ , 20% is due to CFCs and remaining 30% is due to other gases.

### Ozone layer depletion –

- (i) The ozone layer present in the stratosphere acts as an ultraviolet absorbant thus protecting the earth from its harmful effect.
- (ii) Depletion/destruction of ozone layer is primarily caused by CFCs (Chlorofluoro carbons) and halons(halocarbons  $\text{C}_x\text{F}_x\text{Br}_x$ )
- (iii) CFCs are heat transfer agents used in refrigerators, air conditioners, fire extinguishers.
- (iv) Halons are antifire agents used in fire extinguishes .
- (v) The CFCs react with ozone and thus cause thinning of ozone layer which permits more UV radiations to reach the surface of earth.

## WATER POLLUTION

Water pollution is defined as the addition of some substances (organic, inorganic , biological, radio logical) or factor (eg. heat) which degrades the quality of water so that, it either becomes health hazard or unfit for use.

### Kinds of water pollution –

The water pollution may be physical, chemical or biological.

- (a) **Physical pollution** – It involves the changes in the physical properties of water eg. colour, taste, odour, temperature, turbidity etc.
- (b) **Chemical pollution** – It is caused due to change in the chemical properties of water. They mainly include the pH, dissolved  $\text{O}_2$ , inorganic or organic chemicals, heavy metals etc.  
Inorganic chemicals include fluorides, chlorides, phosphates and nitrates. Organic chemicals include phenols, dyes, pesticides and chlorocompounds.
- (c) **Biological pollution** – It is caused due to the presence of living organisms in water such as algae, fungi, bacteria, viruses, protozoans, insects etc.

### Sources of water pollution and effects of water pollutants –

Water pollution is a serious health hazards in India, especially in villages. It is estimated that 50-60% of Indian population suffers from diseases caused by it. 30-40% of all deaths are believed to be due to it.



The principal sources of water pollution and effects of water pollutants are as follows.

#### **Domestic wastes and sewage**

- (i) Sewage containing human faeces, urine, kitchen and cloth washings, organic waste, industrial waste etc. is usually poured into water bodies which cause water pollution.
- (ii) The villagers often wash their animals, cloths and take bath in the same pond. Such water get contaminated with infectious agents for cholera, typhoid, dysentery, Jaundice and skin diseases.
- (iii) Sewage provide food for decomposers, so the population of decomposers increases.
- (iv) Decomposers/microorganisms causing decomposition of sewage take up most of the oxygen present dissolved in water. So in this water BOD (Biological oxygen demand or Biochemical oxygen demand) increased very much.
- (v) BOD is the amount of oxygen in milligrams required by microorganisms for five days to metabolise waste present in one litre of water at 20°C .

#### **Industrial effluents (or industrial discharges)**

Industries usually discharge waste water into ponds, lakes and rivers. Industrial waste water contains heavy metals (mercury, lead, copper, arsenic and cadmium), inorganic pollutants (acids, alkalies and bleaching liquors), organic pollutants (phenol, naphtha, proteins, aromatic compounds, cellulose fibres etc.) Industrial effluents are the most hazardous pollutants on land and water.

##### **(a) Mercury (Hg) –**

- (i) It is released during combustion of coal, smelting of metallic ores, paper and paint industries.
- (ii) Mercury is highly persistent . In water it gets changed into water soluble dimethyl form  $[(CH_3)_2Hg]$  and enters the food chain (undergoes biomagnification).
- (iii) It kills fish and poisons the remaining fauna. Human beings feeding on such poisoned animals develop a crippling deformity called **minamata disease** which is characterised by impairment of various senses, diarrhoea, haemolysis, meningitis and death.
- (iv) The minimata disease was first detected in Japan.
- (v) Mercury inhibits chromosomal disjunction during gamete formation. So it brings about genetic changes also.

##### **(b) Lead (Pb) –**

- (i) The sources of lead pollution are smelters, battery industry, paint, chemical and pesticide industry, automobiles exhausts etc.
- (ii) Lead is pollutant of air, soil and water.
- (iii) It is used as anti-knock reagent in petrol and released by automobile exhausts.
- (iv) Lead is a persistant pollutant and may show biological amplification or biomagnification.
- (v) It is a mutagenic and causes anemia, headache, vomitting, colic, loss of muscle power, bluish lines around the gums, loss of appetite and damage of liver, kidney and brain.

##### **(c) Cadmium (Cd) –**

- (i) It is added to the environment by metal industries, welding and electroplating, pesticides and phosphate industries.
- (ii) Cd shows biological amplification and accumulates inside kidneys, liver, pancreas and spleen.
- (iii) It causes hypertension, anemia, diarrhoea and damages liver and kidneys.

**Oil**

- (i) During extraction and transportation of oil from the sea to different parts, some of the oil spreads over the surface of water. Refineries also discharge a lot of oil present in their effluents into rivers.
- (ii) Oil spreading on the surface of water prevents its oxygenation and inhibits photosynthetic activity of aquatic plants. Animal life is destroyed due to reduced availability of oxygen, food and toxic effects of oil.
- (iii) Oil spilled over the surface of water may catch fire and hence kill all organic life.

**Thermal pollution**

- (i) Hot water is produced by many industries, power generation plants and thermal power plants.
- (ii) Thermal pollution is caused by addition of hot water effluents in water bodies, it brings about rise in water temperature.
- (iii) Warmer water contains less oxygen. Therefore, there is decrease in the rate of decomposition of organic matter.
- (iv) In hot water green algae are replaced by less desirable blue green algae.
- (v) Many organisms fail to reproduce in hot water e.g. Salmon, Trout.

**SOIL POLLUTION**

- (i) Unfavourable alteration of soil by addition or removal of substances and factors which decrease soil productivity, quality of plant products and ground water is called soil pollution.
- (ii) The soil pollutants include pesticides, fertilizers, industrial wastes, salts, radio-nuclides, tin, iron, lead, copper, mercury, aluminium, plastics, paper, glass, broken bottles, discarded food etc.

**Types of Soil pollution**

Soil pollution is of two main types

Negative soil pollution

Positive soil pollution

**Negative soil pollution –**

- (i) It includes over use of soil and erosion.
- (ii) Soil erosion is caused by water and wind.
- (iii) Water erosion of soil is found near the hills where high speed flooding removes top soil.
- (iv) Soil erosion also occurs by high speed winds which bring sand particles from dry desert.

**Positive soil pollution –** It is caused by addition of undesirable substances (eg. pesticides, fertilizers, industrial waste, air pollutant washed down from atmosphere through rain)

**(A) Pesticides –**

- (i) These include insecticides (kill insects), fungicides (kill fungi), algicides (kill algal blooms), weedicides or herbicides (kill weeds), rodenticides (kill rodents).
- (ii) Pesticides are generally broad-spectrum and affect other animals, man and even plants. They are hence, also called **biocides**.
- (iii) DDT (dichloro diphenyl trichloroethane), BHC (benzene hexachloride or gamaxine), aldrin, dieldrin, endrin, heptachlor etc. are chlorinated hydrocarbons used as pesticides.



- (iv) Dieldrin is five times more toxic than DDT when ingested and 40 times more poisonous when absorbed.
- (v) Endrin is the most toxic amongst chlorinated hydrocarbons.

**(B) Fertilizers –**

- (i) The fertilizers contain plant nutrients particularly N,P and K , but the soil also gets polluted mainly due to organic pollutants present as impurities.
- (ii) Excessive use of fertilizers cause soil deterioration through decrease of natural microflora ( nitrogen fixing, nitrifying bacteria)
- (iii) Fertilizers added to soil enter the crop plants. Nitrogen fertilizers produce toxic concentration of nitrate in the leaves and fruits. When these leaves and fruits are eaten, nitrates changed into nitrites by the activity of bacteria in the alimentary canal. The nitrites enter the blood and combine with haemoglobin to form methaemoglobin. As a result oxygen transport is reduced. It gives rise to disease known as **methaemoglobinaemia**. In infants it produces **cyanosis (blue baby syndrome)**

**(C) Industrial wastes –**

- (i) Wastes of the industries are dumped over the soil. They contain a number of toxic substances including cyanides, acids, chromates, alkalies and metals like mercury, copper, zinc, lead, cadmium etc.
- (ii) The industrial pollutants increase the toxicity level of the soil.
- (iii) Heavy metals destroy useful micro organisms of the soil.
- (iv) In 1970 some 200 people died in Japan by Cd pollution of soil due to **itai-itai disease**.

## **NOISE POLLUTION**

- (i) Various kinds of undesirable loud sounds, which disturb our environment are called noise pollutants.
- (ii) Noise pollution is produced by loud sounds of various machines, loudly played radio, automobiles, thundering of jet planes, loud speakers etc.
- (iii) The intensity of noise is measured in decibels (or dB).
- (iv) The sound above 80 dB causes noise pollution.
- (v) Moderate conversation produces 60 dB sound, loud conversation 70dB.

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## SOLVED EXAMPLES

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**Q.1** Eutrophication causes reduction in-

- (A) Dissolved salts (B) Dissolved hydrogen  
(C) Dissolved oxygen (D) All the above

**Ans.** (C)

**Sol.** Dissolved oxygen

**Q.2** The smog is essentially caused by the presence of

- (A)  $O_2$  and  $O_3$   
(B) Oxides of sulphur and nitrogen  
(C)  $O_2$  and  $N_2$   
(D)  $O_3$  and  $N_2$

**Ans.** (B)

**Sol.** Oxides of sulphur and nitrogen

**Q.3** Which are quantitative pollutants out of the following

- (A)  $CO_2$  (B)  $P_2O_5$  (C)  $N_2O_5$  (D)  $NO_2$

**Ans.** (A)

**Sol.**  $CO_2$  become pollutants only when their concentration reaches beyond a threshold value in the environment.

**Q.4** Which are secondary pollutants in the following

- (A)  $O_3$  (B)  $CO_2$  (C) CO (D)  $Cl_2$

**Ans.** (A)

**Sol.** These are formed by reaction between primary pollutants in the presence of sunlight.

**Q.5** Which have Non-biodegradable pollutants in the following

- (A) DDT (B) Domestic sweage (C)  $CO_2$  (D)  $NO_2$

**Ans.** (A)

**Sol.** Pollutants which are not decomposed or degraded by living organisms or micro-organism.



## REDOX REACTIONS

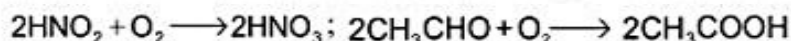
A chemical reaction is a process that leads to the transformation of one set of chemical substances to another substance. Classically, chemical reactions encompass changes that strictly involve the motion of electron in the forming and breaking of chemical bonds. The concept of electron transfer can easily explain in the redox reactions in the case of ionic substances. However, for covalent compounds we use a new term oxidation number to explain oxidation and reduction or redox reactions. Redox reactions are the chemical reactions which involve both oxidation as well as reduction simultaneously. In fact, oxidation and reduction go hand in hand.

### OXIDATION AND REDUCTION

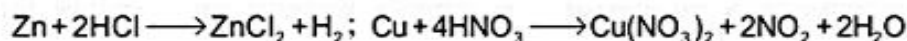
#### Classical Concept :

##### (A) Oxidation

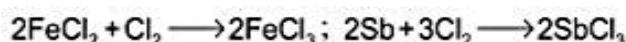
- (i) Oxidation is a chemical reaction in which oxygen is added



- (ii) Hydrogen is removed i.e. hydrogen becomes less



- (iii) Electronegative element is added



- (iv) Electropositive element is removed



##### (B) Reduction

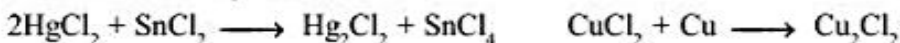
- (i) Addition of Hydrogen.



- (ii) Loss of Oxygen.



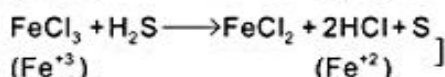
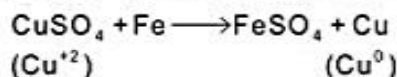
- (iii) Addition of electropositive element.



- (iv) Loss of electronegative element.



- (v) Valency of electropositive element decreases.

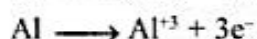
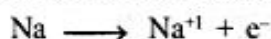


#### Modern Concept :

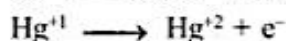
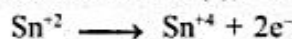
##### (A) Oxidation

The reaction in which an element or an atom or an ion or molecule loses electron(s) is called **oxidation**. Illustrative examples in various cases are given below.

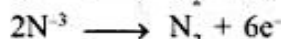
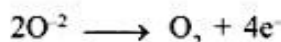
- (i) **Neutral atom** : When a neutral atom loses electron(s), it gets converted to a positive ion.



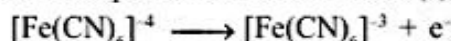
- (ii) **Cation** : When a cation loses electron(s), there is an increase in its positive charge.



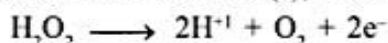
- (iii) **Anion** : When an anion loses electron(s) equal to its negative charge, it gets converted to a neutral atom.



- (iv) **Complex Anion** : When a complex anion loses electron(s), its negative charge decreases.



- (v) **Molecule** : When a molecule loses electron(s), it breaks up into its constituents.



**Note** : In oxidation reactions – Positive charge increases and negative charge decreases.

## (B) Reduction

The reaction in which an element or an atom or an ion (positive or negative) or a molecule accepts electron(s), is called **reduction**. Illustrative examples in various cases are given below.

- (i) **Neutral Atom** : When a neutral element or atom accepts electron(s), it gets converted into an anion.



- (ii) **Cation** : When a cation accepts electron(s) equal to its charge, it gets converted into a neutral atom.



- (iii) Similarly, when a cation accepts electron(s) then, its positive charge decreases. For example



- (iv) **Anion** : When an anion accepts electron(s), its negative charge increases.



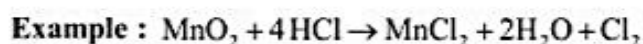
- (v) **Molecule** : When a molecule accepts electron(s), it is a reduction reaction.



**Note** : In reduction reactions – Positive charge decreases and negative charge increases.

## BASIC TERMS

- (1) **Molecular equations** : When the reactants and products involved in a chemical change are written in molecular forms in the chemical equation, it is termed as molecular equation.



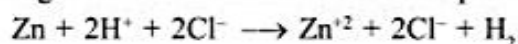
In above example the reactants and products have been written in molecular forms, thus the equation is termed as molecular equation.

- (2) **Ionic equations :** When the reactants and products involved in a chemical change are ionic compounds, these will be present in the form of ions in the solution. The chemical change is written in ionic forms in chemical equation, it is termed as ionic equation. Example,



In above example the reactants and products have been written in ionic forms, thus the equation is termed as ionic equation.

- (3) **Spectator Ions :** Species that are present in the solution but not take part in the reaction and are also omitted while writing the net ionic reaction are called spectator ions or bystander ions.



In this reaction ions are omitted and are called as spectator ions and appear on the reactant as well as product side.

- (4) **Oxidising agent :** The substance (atom, ion or molecule) that gains electrons and is thereby reduced to a low valency state is called an oxidising agent.
- (5) **Reducing agent :** The substance that loses electrons and is thereby oxidised to a higher valency state is called a reducing agent.

## TYPES OF REDOX REACTIONS

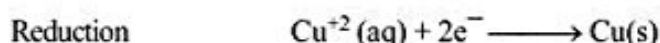
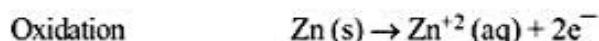
- (1) **Direct and Indirect redox reactions :**

Direct redox reaction : When both oxidation and reduction reactions occurs in same vessel

Indirect Redox reaction : When oxidation and reduction reactions occur in different vessels.

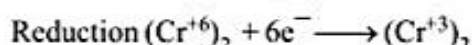
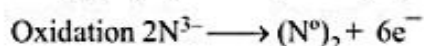
- (2) **Inter molecular redox reactions**

Two substances react one of them is oxidant and other is reductant.



- (3) **Intra-molecular redox reactions**

One element of a compound is oxidised and other element of the same compound is reduced.

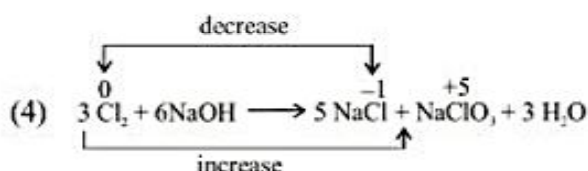
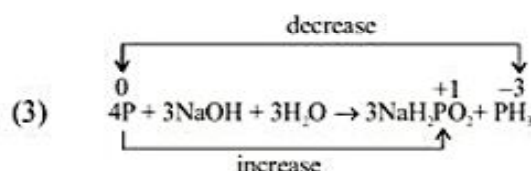
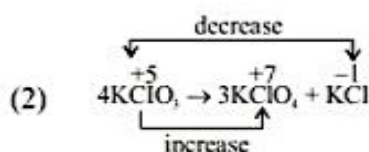
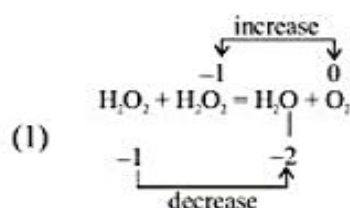




#### (4) Disproportionation

One and the same substance may act simultaneously as an oxidising agent and as a reducing agent with the result that a part of it gets oxidised to a higher state and rest of it is reduced to lower state of oxidation. Such a reaction, in which a substance undergoes simultaneous oxidation and reduction is called disproportionation and the substance is said to disproportionate.

Following are the some examples of disproportionation,



#### (5) Comproportionation reaction



Nitrogen in this compound has -3 and +3 oxidation number so it is not a definite value, so its not a disproportion reaction. It is an example of comproportionation reaction which is a case of redox reaction in which a element from two different oxidation state gets converted into a single oxidation state.

## OXIDISERS AND REDUCERS

### Oxidizers

Substances that have the ability to oxidize other substances are said to be oxidative or oxidizing and are known as oxidizing agents, oxidants, or oxidizers. Put another way, the oxidant (oxidizing agent) removes electrons from another substance; i.e., it oxidizes other substances, and is thus itself reduced. And, because it "accepts" electrons, it is also called an electron acceptor.

Oxidants are usually chemical elements or substances with elements in high oxidation states

#### Important oxidising agents

- (i) Molecules made up of electronegative elements.  
Example :  $\text{O}_2$ ,  $\text{O}_3$  and  $\text{X}_2$  (halogens).
- (ii) Compounds containing an element which is in the highest oxidation state.  
Example :  $\text{KMnO}_4$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{Na}_2\text{Cr}_2\text{O}_7$ ,  $\text{CrO}_3$ ,  $\text{H}_2\text{SO}_4$ ,  
 $\text{HNO}_3$ ,  $\text{NaNO}_3$ ,  $\text{FeCl}_3$ ,  $\text{HgCl}_2$ ,  $\text{KClO}_4$ ,  $\text{SO}_3$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}_2$  etc.
- (iii) Oxides of elements,  $\text{MgO}$ ,  $\text{CuO}$ ,  $\text{CrO}_3$ ,  $\text{CO}_2$ ,  $\text{P}_4\text{O}_{10}$ , etc.
- (iv) Fluorine is the strongest oxidising agent.



## Reducers

Substances that have the ability to reduce other substances are said to be reductive or reducing and are known as reducing agents, reductants, or reducers. The reductant (reducing agent) transfers electrons to another substance; i.e., it reduces others, and is thus itself oxidized. And, because it "donates" electrons, it is also called an electron donor. Electron donors can also form charge transfer complexes with electron acceptors.

### Important reducing agents

- (i) All metals e.g. Na, Zn, Fe, Al, etc.
- (ii) A few non-metals e.g. C, H<sub>2</sub>, S etc.
- (iii) Hydracids : HCl, HBr, HI, H<sub>2</sub>S etc.
- (iv) A few compounds containing an element in the lower oxidation state (ous).  
Example : FeCl<sub>2</sub>, FeSO<sub>4</sub>, SnCl<sub>2</sub>, Hg<sub>2</sub>Cl<sub>2</sub>, Cu<sub>2</sub>O etc.
- (v) Metallic hydrides e.g. NaH, LiH etc.
- (vi) Organic compounds like HCOOH and (COOH)<sub>2</sub> and their salts, aldehydes, alkanes etc.
- (vii) Lithium is the strongest reducing agent in solution.
- (viii) Cesium is the strongest reducing agent in absence of water.

### Substances which act as oxidising as well as reducing agents

Examples : H<sub>2</sub>O<sub>2</sub>, SO<sub>2</sub>, H<sub>2</sub>SO<sub>3</sub>, HNO<sub>2</sub>, NaNO<sub>2</sub>, Na<sub>2</sub>SO<sub>3</sub>, O<sub>3</sub> etc.

### Tips for the identification of oxidising and reducing agents

- (i) If an element is in its highest possible oxidation state in a compound, the compound can function as an oxidising agent.  
Example : KMnO<sub>4</sub>, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, HClO<sub>4</sub> etc.
- (ii) If an element is in its lowest possible oxidation state in a compound, the compound can function only as a reducing agent.  
Example : H<sub>2</sub>S, H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, FeSO<sub>4</sub>, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, SnCl<sub>2</sub> etc.
- (iii) If an element is in its intermediate oxidation state in a compound, the compound can function both as an oxidising agent as well as reducing agent.  
Example : H<sub>2</sub>O<sub>2</sub>, H<sub>2</sub>SO<sub>3</sub>, HNO<sub>2</sub>, SO<sub>2</sub> etc.
- (iv) If a highly electronegative element is in its highest oxidation state in a compound, that compound can function as a powerful oxidising agent.  
Example : KClO<sub>4</sub>, KClO<sub>3</sub>, KBrO<sub>3</sub>, KIO<sub>3</sub> etc.
- (v) If an electronegative element is in its lowest possible oxidation state in a compound or in free state, it can function as a powerful reducing agent.  
Example : I<sup>-</sup>, Br<sup>-</sup>, N<sup>3-</sup> etc.

**Illustration**

---

1. Which of the following acts as both oxidant and reductant –



Ans. B

Sol. O.N. of N in  $\text{HNO}_2$  is + 3

Max. O.N. of N is + 5

Min. O.N. of N is – 3

Thus O.N. of N in  $\text{HNO}_2$  can show an increase or decrease as the case may be. That is why  $\text{HNO}_2$  acts as oxidant and reductant both.

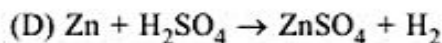
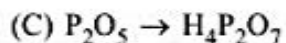
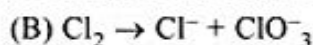
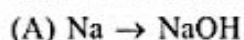
O.N. of N in  $\text{HNO}_3$  is + 5, Hence it can act only as an oxidant.

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**Exercise**

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1. State which of the following reactions is neither oxidation nor reduction –



Ans. C

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**OXIDATION NUMBER (O.N.)****Definition :**

Oxidation number of an element in a particular compound represents the number of electrons lost or gained by an element during its change from free state into that compound or Oxidation number of an element in a particular compound represents the extent of oxidation or reduction of an element during its change from free state into that compound.

Oxidation number is given positive sign if electrons are lost. Oxidation number is given negative sign if electrons are gained. Oxidation number represents real charge in case of ionic compounds, however, in covalent compounds it represents for imaginary charge.

**Rule for deriving Oxidation Number**

Following arbitrary rules have been adopted to derive Oxidation Number of elements on the basis of periodic properties of elements.

1. In uncombined state or free state, Oxidation Number of an element is zero.
-

2. In combined state Oxidation Number of .....
- ..... F is always  $-1$ .
  - ..... O is  $-2$ ; In peroxides ( $-O-O-$ ) it is  $-1$ . However in  $F_2O$ , it is  $+2$ .
  - ..... H is  $1$ ; In ionic hydrides it is  $-1$ .
  - ..... metals is always positive.
  - ..... alkali metals (IA e.g. Li, Na, K, Rb, Cs, Fr) is always  $+1$ .
  - ..... alkaline earth metals (IIA e.g. Be, Mg, Ca, Sr, Ba, Ra) is always  $+2$ .
  - ..... halogens in halides is always  $-1$ .
  - ..... sulphur in sulphides in always  $-2$ .
3. The algebraic sum of all the Oxidation Number of elements in a compound is equal to zero. e.g.  $K_2MnO_4$   
 $2 \times \text{Oxidation Number of K} + \text{Oxidation Number of Mn} + 4 (\text{Oxidation Number of O}) = 0$
4. The algebraic sum of all the Oxidation Numbers of elements in a radical is equal to net charge on that radical  
 e.g.  $C_2O_4^{2-}$ .  $2 \times \text{Oxidation Number of C} + 4 (\text{Oxidation Number of O}) = -2$ .
5. Variable oxidation number is most commonly shown by transition elements as well as by p-block elements.

**Transition elements :** Fe ( $+2$  &  $+3$ ), Cu ( $+1$  &  $+2$ ), Mn ( $+7$ ,  $+6$ ,  $+5$ ,  $+4$ ,  $+3$ ,  $+2$ ,  $+1$ ) etc.

**p-block elements :** As ( $+3$  &  $+5$ ); Sb ( $+3$  &  $+5$ ), Sn ( $+2$  &  $+4$ ) etc.

Group No.	Outer shell configuration	Common Oxidation Number
1	$ns^1$	0, $+1$
2	$ns^2$	0, $+2$
13	$ns^2 np^1$	0, $+1$ , $+3$
14	$ns^2 np^2$	0, $\pm 1$ , $\pm 2$ , $\pm 3$ , $\pm 4$
15	$ns^2 np^3$	0, $\pm 1$ , $\pm 3$ , $+5$
16	$ns^2 np^4$	0, $\pm 2$ , $+4$ , $+6$
17	$ns^2 np^5$	0, $\pm 1$ , $+3$ , $+5$ , $+7$
18	$ns^2 np^6$	0 (usually)

### Exceptions

- Oxidation Number of Cl in  $Cl_2O$  is  $+1$ , because Cl acts as an electropositive element in this.
- Oxidation Number of Cl in  $ClF_3$  =  $+3$
- Oxidation Number of Cl in  $KClO_3$  =  $+5$
- Oxidation Number of I in  $IF_7$  =  $+7$
- Oxidation Number of I in  $IF_5$  =  $+5$
- Oxidation Number of Cl in  $Cl_2O_7$  =  $+7$
- Oxidation Number of Cl in  $HClO$  =  $+1$
- Oxidation Number of Cl in  $HClO_2$  =  $+5$
- Oxidation Number of Cl in  $HClO_3$  =  $+5$
- Oxidation Number of Cl in  $HClO_4$  =  $+7$



### Oxidation Number of Radicals

Oxidation Number of radicals is equal to charge present on them. For example,

- (i) Oxidation Number of sulphite ( $\text{SO}_3^{-2}$ ), sulphate ( $\text{SO}_4^{-2}$ ), thiosulphate ( $\text{S}_2\text{O}_3^{-2}$ ), oxalate ( $\text{C}_2\text{O}_4^{-2}$ ), carbonate ( $\text{CO}_3^{-2}$ ), sulphide ( $\text{S}^{-2}$ ) is equal to charge ( $-2$ ) present on each of them.
- (ii) Oxidation Number of each of the anions,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{NO}_3^-$ ,  $\text{CN}^-$ ,  $\text{OH}^-$ ,  $\text{SCN}^-$ ,  $\text{CH}_3\text{COO}^-$  and  $\text{HCO}_3^-$  is  $-1$ .
- (iii) Oxidation Number of each of the anions,  $\text{PO}_4^{-3}$ ,  $\text{BO}_3^{-3}$ ,  $\text{AsO}_4^{-3}$ . (Arsenate) and  $\text{AsO}_3^{-3}$  (Arsenite) is  $-3$ .
- (iv) Oxidation Number of each of the cations,  $\text{CH}_3^+$ ,  $\text{NH}_4^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$  is  $+1$ .
- (v) Oxidation Number of each of the cations,  $\text{Ca}^{+2}$ ,  $\text{Mg}^{+2}$ ,  $\text{Sr}^{+2}$  and  $\text{Fe}^{+2}$  is  $+2$ .
- (vi) Oxidation Number of Al in  $[\text{Al}(\text{H}_2\text{O})_6]^{+3}$  is  $+3$ .

### Oxidation no. of S element

1.	S in $\text{H}_2\text{S}$	$2(1) + x = 0$	$+2 + x = 0$	$x = -2$
2.	S in $\text{SO}_2$	$x + 2(-2) = 0$	$x - 4 = 0$	$x = +4$
3.	S in $\text{SO}_4^{-2}$	$x + 4(-2) = -2$	$x - 8 = -2$	$x = +6$
4.	S in $\text{SO}_3^{-2}$	$x + 3(-2) = -2$	$x - 6 = -2$	$x = +4$
5.	S in $\text{SF}_6$	$x + 6(-1) = 0$	$x - 6 = 0$	$x = +6$
6.	S in $\text{H}_2\text{SO}_3$	$2(-1) + x + 3(-2) = 0$	$+2 + x - 6 = 0$	$x = +4$

### Oxidation no. of P element

1. Oxidation number of P in  $\text{P}_4 = 0$
2. P in  $\text{PO}_4^{-3}$  :  $x + 4(-2) = -3$ ,  $x = +5$
3. P in  $\text{NaHPO}_2$  :  $1(1) + 1(1) + 2(-2) = 0$ ,  $x = +2$
4. P in  $\text{H}_3\text{PO}_3$  :  $3(+1) + x + 3(-2) = 0$ ,  $x = +3$
5. P in  $\text{Na}_2\text{HPO}_4$  :  $2(1) + 1(1) + x + 4(-2) = 0$ ,  $x = +5$
6. P in  $\text{Mg}_2\text{P}_2\text{O}_7$  :  $2(2) + 2x + 7(-2) = 0$ ,  $2x = 10$ ,  $x = +5$

### Oxidation Number of Cr in its various compounds

1. Cr in  $\text{CrO}$  :  $x - 2 = 0$ ,  $x = +2$
2. Cr in  $\text{Cr}_2\text{O}_3$  :  $2x - 6 = 0$ ,  $x = +3$
3. Cr in  $\text{CrSO}_4$  :  $x - 2 = 0$ ,  $x = +2$
4. Cr in  $\text{Cr}_2(\text{SO}_4)_3$  :  $2x - 6 = 0$ ,  $x = +3$
5. Cr in  $\text{CrO}_2\text{Cl}_2$  :  $2x - 6 = 0$ ,  $x = +3$
6. Cr in  $\text{K}_2\text{Cr}_2\text{O}_7$  :  $2 + 2x - 14 = 0$ ,  $x = +6$
7. Cr in  $\text{K}_2\text{CrO}_4$  :  $2 + x - 8 = 0$ ,  $x = +6$
8. Cr in  $\text{Cr}_2\text{O}_7^{-2}$  :  $2x - 14 = -2$ ,  $2x = 12$ ,  $x = +6$
9. Cr in  $\text{CrO}_4^{-2}$  :  $x - 8 = -2$ ,  $x = +6$
10. Cr in  $\text{Cr}(\text{NH}_3)_4\text{SO}_4$  :  $x - 2 = 0$ ,  $x = +2$  (Here, Oxidation Number of  $\text{NH}_3$  is zero)
11. Oxidation Number of Cr in  $[\text{Cr}(\text{NH}_3)_4]^{+2}$  :  $x = +2$
12. Oxidation Number of Cr in  $\text{Na}_2\text{CrO}_4$  :  $+2 + x - 8 = 0$ ,  $x = +6$
13. Oxidation Number of Cr in  $\text{Cr}(\text{CO})_6$  :  $x = 0$  (Oxidation Number of Cr = 0)



### Oxidation Number of Mn in its compounds

1.	Mn in MnO	: $x - 2 = 0$ ,	$x = + 2$
2.	Mn in $\text{Mn}_2\text{O}_3$	: $2x - 6 = 0$ ,	$x = + 3$
3.	Mn in $\text{MnSO}_4$	: $x - 2 = 0$ ,	$x = + 2$
4.	Mn in $\text{Mn}_2(\text{SO}_4)_3$	: $2x - 6 = 0$ ,	$x = + 3$
5.	Mn in $\text{K}_2\text{MnO}_4$	: $+2 + x - 8 = 0$ ,	$x = + 6$
6.	Mn in $\text{KMnO}_4$	: $+1 + x - 8 = 0$ ,	$x = + 7$
7.	Mn in $\text{Mn}(\text{CO})_{10}$	: $x + 10(0) = 0$	$x = 0$
8.	Mn in $\text{MnO}_4^-$	: $x - 8 = -1$	$x = + 7$
9.	Mn in $\text{Mn}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$	: $x - 4 = 0$ ,	$x = + 4$

### Comparison of Valency and Oxidation number

Valency of an element represents the power or capacity of the element to combine with the other element. The valency of an element is numerically equal to the number of hydrogen atoms or chlorine atoms or twice the number of oxygen atoms that combine with one atom of that element. It is also equal to the number of electrons lost or accepted or shared by the atoms of an element.

In some cases (mainly in the case of electrovalent compounds), valency and oxidation number are the same but in other cases they may have different values. The difference between the two have been tabulated.

S.No.	Valency	Oxidation number (State)
1.	It is the combining capacity of the element. No plus or minus sign is attached to it.	Oxidation number is the charge (real or imaginary) present on the atom of the element when it is in combination. It may have plus or minus sign.
2.	Valency of an element is usually fixed.	Oxidation number of an element may have different values. It depends on the nature of compound in which it is present.
3.	Valency is always a whole number.	Oxidation number of the element may be a whole number or fractional.
4.	Valency of the element is never zero except in noble gases.	Oxidation number of the element may be zero.

In the following compounds of carbon, the oxidation number varies from  $-4$  to  $+4$  but valency of carbon is 4 in all the compounds.

Compound	$\text{CH}_4$	$\text{CH}_3\text{Cl}$	$\text{CH}_2\text{Cl}_2$	$\text{CHCl}_3$	$\text{CCl}_4$
Oxidation number of carbon	$-4$	$-2$	$0$	$+2$	$+4$

### OXIDATION AND REDUCTION IN TERMS OF OXIDATION NUMBER

- (1) **Oxidation** : Chemical process involving increase in oxidation number.
- (2) **Reduction** : Chemical process involving decrease in oxidation number.
- (3) **Oxidising agent** : substance which undergoes decrease in oxidation number of one or more of its element.
- (4) **Reducing agent** : Substance which undergoes increase in oxidation number of one or more of its elements.

## (5) List of some common oxidising agents :

Reagent	Chemical change	Element Changing O.N.	Change in O.N.
$F_2$	$F_2 \rightarrow 2F^-$	F	$0 \rightarrow -1$
$O_3$	$O_3 \rightarrow H_2O$	O	$0 \rightarrow -2$
$H_2O_2$	$H_2O_2 \rightarrow H_2O$	O	$-1 \rightarrow -2$
$KMnO_4 / H_2SO_4$	$MnO_4^- \rightarrow MnO_4^{2-}$	Mn	$+7 \rightarrow +2$
$KMnO_4 / KOH$	$MnO_4^- \rightarrow MnO_4^{2-}$	Mn	$+7 \rightarrow +6$
$KMnO_4 / H_2O$	$MnO_4^- \rightarrow MnO_2$	Mn	$+7 \rightarrow +4$
Conc. $HNO_3$	$HNO_3 \rightarrow NO_2$	N	$+5 \rightarrow +4$
$K_2Cr_2O_7 / H_2SO_4$	$Cr_2O_7^{2-} \rightarrow Cr^{3+}$	Cr	$+6 \rightarrow +3$
$KIO_3 / HCl$	$IO_3^-$	I	$+5 \rightarrow -1$

## (6) List of some common reducing agents:

Reagent	Chemical Change	Element changing O.N.	Change in O.N.
Metal atoms	$M \rightarrow M^{n+}$	M	$0 \rightarrow +n$
Alkali metals	$M \rightarrow M^+$	M	$0 \rightarrow +1$
Carbon	$C \rightarrow CO_2$	C	$0 \rightarrow +4$
$S_8$	$S_8 \rightarrow SO_2$	S	$0 \rightarrow +4$
$S_2O_3^{2-}$	$S_2O_3^{2-} \rightarrow S_4O_6^{2-}$	S	$+2 \rightarrow +2.5$
$KI$	$I^- \rightarrow I_2$	I	$-1 \rightarrow 0$
$C_2O_4^{2-}$	$C_2O_4^{2-} \rightarrow CO_2$	C	$+3 \rightarrow +4$
$H_2S$	$H_2S \rightarrow S$	S	$-2 \rightarrow 0$

(7) Metal ions in their lowest oxidation states such as  $Fe^{2+}$ ,  $Sn^{2+}$ ,  $Cu^+$ , etc., also act as reducing agents.

**Common Oxidising and Reducing Agents.**

Oxidising agent	Effective Change	Decrease in O.N.
$KMnO_4$ in acid solution	$MnO_4^- \rightarrow Mn^{2+}$	5
$KMnO_4$ in alkaline solution	$MnO_4^- \rightarrow MnO_2$	3
$K_2Cr_2O_7$ in acid solution	$Cr_2O_7^{2-} \rightarrow Cr^{3+}$	3
dilute $HNO_3$	$NO_3^- \rightarrow NO$	3
concentrated $HNO_3$	$NO_3^- \rightarrow NO_2$	1
concentrated $H_2SO_4$	$SO_4^{2-} \rightarrow SO_2$	2
manganese (IV) oxide	$MnO_2 \rightarrow Mn^{2+}$	2
chlorine	$Cl \rightarrow Cl^-$	1
chloric (I) acid	$ClO^- \rightarrow Cl^-$	2
$KIO_3$ in dilute acid	$IO_3^- \rightarrow I$	5
$KIO_3$ in concentrated acid	$IO_3^- \rightarrow I^-$	4

Reducing agent	Effective Change	Increase in O.N.
iron(II) salts (acid)	$\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$	1
tin (II) salts (acid)	$\text{Sn}^{2+} \rightarrow \text{Sn}^{4+}$	2
sulphites (acid)	$\text{SO}_3^{2-} \rightarrow \text{SO}_4^{2-}$	2
hydrogen sulphide	$\text{S}^{2-} \rightarrow \text{S}$	2
iodides (dilute acid)	$\text{I}^- \rightarrow \text{I}$	1
iodides (concentrated acid)	$\text{I}^- \rightarrow \text{I}^+$	2
metals, e. g. Zn	$\text{Zn} \rightarrow \text{Zn}^{2+}$	2
hydrogen	$\text{H} \rightarrow \text{H}^+$	1

**Special cases of ON :** Apart from above discussed molecules there are some special cases due to peroxide linkage or covalent or coordinate bond, the following rules are generally used.

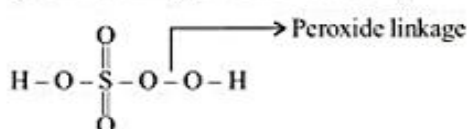
**Type I.** In molecules containing peroxide linkage in addition to element-oxygen bonds. For example,

- (i) Oxidation number of S in  $\text{H}_2\text{SO}_5$   
(Permonosulphuric acid or Caro's acid)

By usual method;  $\text{H}_2\text{SO}_5$

$$2 \times 1 + x + 5 \times (-2) = 0 \text{ or } x = +8$$

But this cannot be true as maximum oxidation number for S cannot exceed +6. Since S has only 6 electrons in its valence shell. This exceptional value is due to the fact that two oxygen atoms in shows peroxide linkage as shown below,



Therefore the evaluation of o.n. of sulphur here should be made as follows,

$$\begin{array}{cccc} 2 \times (+1) & + & x & + & 3 \times (-2) & + & 2 \times (-1) \\ \text{(for H)} & \text{(for S)} & \text{(for O)} & \text{(for O-O)} & & & \\ \text{or } 2 & + & x & - & 6 & - & 2 = 0 \quad \text{or} \quad x = +6. \end{array}$$

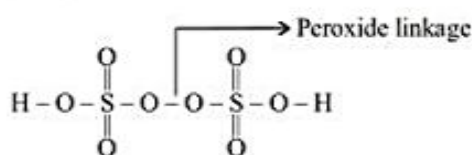
- (ii) Oxidation number of S in  $\text{H}_2\text{S}_2\text{O}_8$   
(Peroxidisulphuric acid or Marshall's acid)

By usual method;  $\text{H}_2\text{S}_2\text{O}_8$

$$1 \times 2 + 2x + 8(-2) = 0$$

$$2x = +16 - 2 = 14 \text{ or } x = +7$$

Similarly Caro's acid, Marshall's acid also has a peroxide linkage so that in which S shows +6 oxidation state.





Therefore the evaluation of oxidation state of sulphur should be made as follow,

$$2 \times (+1) + 2 \times (x) + 6 \times (-2) + 2 \times (-1) = 0$$

(for H)      (for S)      (for O)      (for O-O)

or  $2 + 2x - 12 - 2 = 0$  or  $x = +6$ .

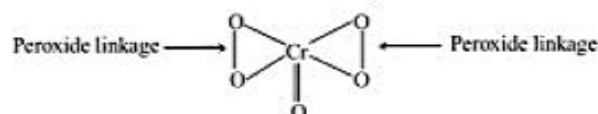
- (iii) Oxidation number of Cr in  $\text{CrO}_5$

(Blue perchromate)

By usual method  $\text{CrO}_5$ ;  $x - 10 = 0$  or  $x = +10$

This cannot be true as maximum O. N. of Cr cannot be more than +6. Since Cr has only five electrons in 3d orbitals and one electron in 4s orbital. This exceptional value is due to the fact that four oxygen atoms in  $\text{CrO}_5$  are in peroxide linkage.

The chemical structure of  $\text{CrO}_5$  is



Therefore, the evaluation of oxidation number of Cr should be made as follows

$$x + 1 \times (-2) + 4 \times (-1) = 0$$

(for Cr)      (for O)      (for O-O)

or  $x - 2 - 4 = 0$  or  $x = +6$ .

**Type II.** In molecules containing covalent and coordinate bonds, following rules are used for evaluating the oxidation numbers of atoms.

- (i) For each covalent bond between dissimilar atoms the less electronegative element is assigned the oxidation number of +1 while the atom of the more electronegative element is assigned the oxidation number of -1.
- (ii) In case of a coordinate-covalent bond between similar or dissimilar atoms but the donor atom is less electronegative than the acceptor atom, an oxidation number of +2 is assigned to the donor atom and an oxidation number of -2 is assigned to the acceptor atom.

Conversely, if the donor atom is more electronegative than the acceptor atom, the contribution of the coordinate bond is neglected. Examples,

- (a) Oxidation number of C in  $\text{HC} \equiv \text{N}$  and  $\text{HN} \equiv \text{C}$

The evaluation of oxidation number of C cannot be made directly by usual rules since no standard rule exists for oxidation numbers of N and C.

In such cases, evaluation of oxidation number should be made using indirect concept or by the original concepts of chemical bonding.

- (i) Oxidation number of carbon in  $\text{H} - \text{N} \equiv \text{C}$

The contribution of coordinate bond is neglected since the bond is directed from a more electronegative N atom (donor) to a less electronegative carbon atom (acceptor).

Therefore the oxidation number of N in  $\text{HN} \equiv \text{C}$  remains -3 as it has three covalent bonds.

$$1 \times (+1) + 1 \times (-3) + x = 0$$

(for H)      (for N)      (for C)

or  $1 + x - 3 = 0$  or  $x = +2$ .

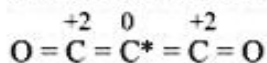
- (ii) Oxidation number of carbon in  $\text{HC} \equiv \text{N}$

In  $\text{HC} \equiv \text{N}$ , N is more electronegative than carbon, each bond gives an oxidation number of -1 to N. There are three covalent bonds, the oxidation number of N is taken as -3

Now  $\text{HC} \equiv \text{N}$   $\therefore +1 + x - 3 = 0 \Rightarrow x = +2$

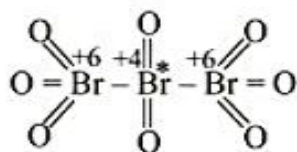


- (b) Oxidation number of carbon in
- $C_3O_2$



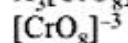
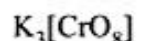
Structure of  $C_3O_2$   
(Carbon suboxide)

- (c) Oxidation number of Br in
- $Br_3O_8$



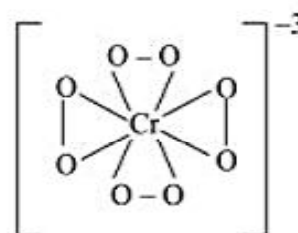
Structure of  $Br_3O_8$  (tribromooctaoxide)

- (d) Oxidation number of Cr in
- $K_3[CrO_8]$



$$x - 8 = -3$$

$$x = 5$$



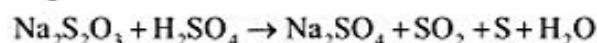
**Type III.** In a molecule containing two or more atoms of same or different elements in different oxidation states.

- (i) Oxidation number of S in
- $Na_2S_2O_3$

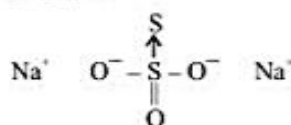
By usual method

$$\therefore 2 \times (+1) + 2 \times x + 3(-2) = 0 \quad \text{or} \quad 2 + 2x - 6 = 0 \quad \text{or} \quad x = 2.$$

But this is unacceptable as the two sulphur atoms in  $Na_2S_2O_3$  cannot have the same oxidation number because on treatment with dil.  $H_2SO_4$ , one sulphur atom is precipitated while the other is oxidised to  $SO_2$ .



In this case, the oxidation number of sulphur is evaluated from concepts of chemical bonding. The chemical structure of  $Na_2S_2O_3$  is



Due to the presence of a co-ordinate bond between two sulphur atoms, the acceptor sulphur atom has oxidation number of -2 whereas the other S atom gets oxidation number of +2.

$$2 \times (+1) + 3 \times (-2) + x \times 1 + 1 \times (-2) = 0$$

$$\text{(for Na)} \quad \text{(for O)} \quad \text{(for S)} \quad \text{(for coordinated S)}$$

$$\text{or } +2 - 6 + x - 2 = 0 \quad \text{or } x = +6$$

Thus two sulphur atoms in  $Na_2S_2O_3$  have oxidation number of -2 and +6.

- (ii) Oxidation number of chlorine in
- $CaOCl_2$

(bleaching powder)

In bleaching powder,  $Ca(OCl)Cl$ , the two Cl atoms are in different oxidation states i.e., one  $Cl^-$  having oxidation number of -1 and the other as  $OCl^-$  having oxidation number of +1.

(iii) Oxidation number of N in  $\text{NH}_4\text{NO}_3$ By usual method  $\text{N}_2\text{H}_4\text{O}_3$ ;  $2x + 4 \times (+1) + 3 \times (-1) = 0$ 

$$2x + 4 - 3 = 0 \quad \text{or} \quad 2x = +1 \quad (\text{wrong})$$

No doubt  $\text{NH}_4\text{NO}_3$  has two nitrogen atoms but one N has negative oxidation number (attached to H) and the other has positive oxidation number (attached to O). Hence the evaluation should be made separately for  $\text{NH}_4^+$  and  $\text{NO}_3^-$

$$\text{NH}_4^+ \quad x + 4 \times (+1) = +1 \quad \text{or} \quad x = -3$$

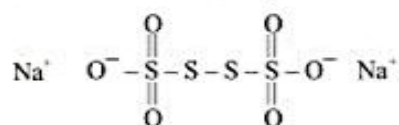
$$\text{NO}_3^- \quad x + 3 \times (-2) = -1 \quad \text{or} \quad x = +5.$$

(iv) Oxidation number of Fe in  $\text{Fe}_3\text{O}_4$ 

In  $\text{Fe}_3\text{O}_4$ , Fe atoms are in two different oxidation states.  $\text{Fe}_3\text{O}_4$  can be considered as an equimolar mixture of  $\text{FeO}$  [iron (II) oxide] and  $\text{Fe}_2\text{O}_3$  [iron (III) oxide]. Thus in one molecule of  $\text{Fe}_3\text{O}_4$ , two Fe atoms are in +3 oxidation state and one Fe atom is in +2 oxidation state.

(v) Oxidation number of S in sodium tetrathionate ( $\text{Na}_2\text{S}_4\text{O}_6$ )

Its structure can be represented as follows,



The two S-atoms which are linked to each other have oxidation number zero. The oxidation number of other S-atoms can be calculated as follows

Let oxidation number of S is x.

$$\begin{array}{lll} 2 \times x & + & 2 \times 0 + 6 \times (-2) = -2 \\ (\text{for S}) & (\text{for S-S}) & (\text{for O}) \\ x = +5. \end{array}$$

### Illustration

1. Determine Oxidation number of the element underlined in each of the following :

(a)  $\underline{\text{Fe}}\text{SO}_4 (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$  :Sol. Put sum of Oxidation Numbers of  $\text{SO}_4 = -2$ Sum of Oxidation Numbers in  $(\text{NH}_4)_2\text{SO}_4 = 0$ Sum of Oxidation Numbers in  $\text{H}_2\text{O} = 0$ 

$$x + (-2) + 0 + 0 = 0;$$

[ $(\text{NH}_4)_2\text{SO}_4$  is a complete molecule][ $\text{H}_2\text{O}$  is complete molecule]

$$\therefore x = +2$$

(b)  $\underline{\text{Fe}}_{0.94}\text{O}$  :Sol.  $x \times 0.94 + (-2) = 0;$ 

$$x = 200/94$$

(c)  $\text{Na}_2[\underline{\text{Fe}}(\text{CN})_5\text{NO}]$  :Sol. NO in iron complexes has  $\text{NO}^+$  nature.

$$\text{Thus} \quad 2 \times 1 + x + 5 \times (-1) + 1 = 0$$

$$(\text{for Na}) \quad (\text{for Fe}) \quad (\text{for CN}) \quad (\text{for NO});$$

$$\therefore x = +2$$

(d)  $\underline{\text{Fe}}\text{NO}(\text{H}_2\text{O})_5\text{SO}_4$  :Sol.  $x + 1 + 5 \times 0 + (-2) = 0;$ 

$$\therefore x = +1$$

### Exercise

1. Oxidation number of Fe in  $[\text{Fe}(\text{CN})_6]^{-3}$ ,  $[\text{Fe}(\text{CN})_6]^{-4}$ ,  $[\text{Fe}(\text{SCN})]^{+2}$  and  $[\text{Fe}(\text{H}_2\text{O})_6]^{+3}$  respectively would be—  
 (A) +3, +2, +3 and +3 (B) +3, +3, +3 and +3 (C) +3, +2, +2 and +2 (D) +2, +2, +2 and +2

Ans. A

## BALANCING OF REDOX REACTIONS

There are a number of methods for balancing oxidation - reduction reactions, two main methods are discussed below :

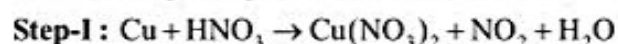
(1) Oxidation number method

(2) Ion - electron method

- (1) **Oxidation number method** : The method for balancing redox reactions by oxidation number change method was developed by Johnson. In a balanced redox reaction, total increase in oxidation number must be equal to the total decrease in oxidation number. This equivalence provides the basis for balancing redox reactions. This method is applicable to both molecular and ionic equations. The general procedure involves the following steps,

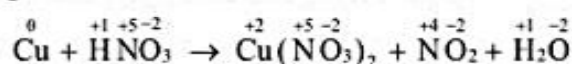
- Write the skeleton equation (if not given, frame it) representing the chemical change.
- Assign oxidation numbers to the atoms in the equation and find out which atoms are undergoing oxidation and reduction. Write separate equations for the atoms undergoing oxidation and reduction.
- Find the change in oxidation number in each equation. Make the change equal in both the equations by multiplying with suitable integers. Add both the equations.
- First balance those substances which have undergone change in oxidation number and then other atoms except hydrogen and oxygen. Finally balance hydrogen and oxygen by putting  $\text{H}_2\text{O}$  molecules wherever needed.  
 The final balanced equation should be checked to ensure that there are as many atoms of each element on the right as there are on the left.
- In ionic equations the net charges on both sides of the equation must be exactly the same. Use  $\text{H}^+$  ion/ions in acidic reactions and  $\text{OH}^-$  ion/ions in basic reactions to balance the charge and number of hydrogen and oxygen atoms.

The following example illustrate the above rules,

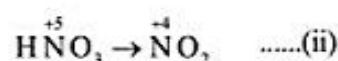
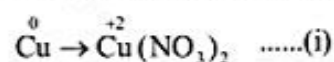


(Skeleton equation)

**Step-II** : Writing the oxidation number of all the atoms.



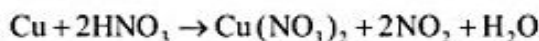
**Step-III** : Change in oxidation number has occurred in copper and nitrogen.



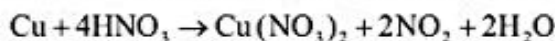


Increase in oxidation number of copper = 2 units per molecule Cu  
 Decrease in oxidation number of nitrogen = 1 unit per molecule  $\text{HNO}_3$

**Step-IV :** To make increase and decrease equal, equation (ii) is multiplied by 2.



**Step-V :** Balancing nitrate ions, hydrogen and oxygen, the following equation is obtained.



This is the balanced equation.

## (2) Ion-electron method (half reaction method)

Jette and LaMev developed the method for balancing redox-reactions by ion electron method in 1927. It involves the following steps

- (i) Write down the redox reaction in ionic form.
- (ii) Split the redox reaction into two half reactions, one for oxidation and other for reduction.
- (iii) Balance each half reaction for the number of atoms of each element. For this purpose,
  - (a) Balance the atoms other than H and O for each half reaction using simple multiples.
  - (b) Add water molecules to the side deficient in oxygen and  $\text{H}^+$  to the side deficient in hydrogen. This is done in acidic or neutral solutions.
  - (c) In alkaline solution, for each excess of oxygen, add one water molecule to the same side and  $2\text{OH}^-$  ions to the other side. If hydrogen is still unbalanced, add one  $\text{OH}^-$  ion for each excess hydrogen on the same side and one water molecule to the other side.
- (iv) Add electrons to the side deficient in electrons as to equalise the charge on both sides.
- (v) Multiply one or both the half reactions by a suitable number so that number of electrons become equal in both the equations.
- (vi) Add the two balanced half reactions and cancel any term common to both sides.

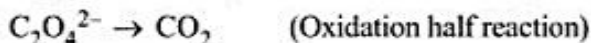
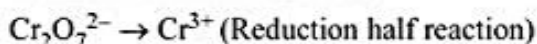
The following examples illustrate the above rules

### In acidic medium

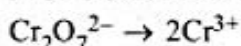
- (a) consider the example,



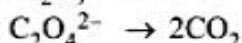
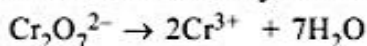
- (b) Write both the half reactions.



- (c) Atoms other than H and O are balanced

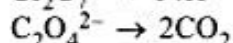
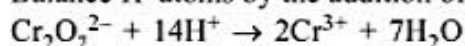


- (d) Balance O-atoms by the addition of  $\text{H}_2\text{O}$  to another side

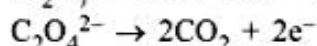
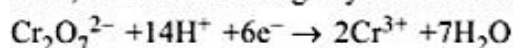




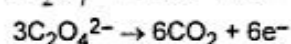
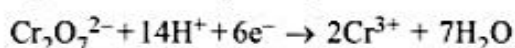
- (e) Balance H-atoms by the addition of  $H^+$  ions to another side



- (f) Now, balance the charge by the addition of electrons ( $e^-$ ).

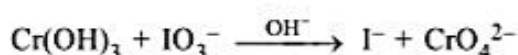


- (g) Multiply equations by a constant to get number of electrons same in both side. In the above case second equation is multiplied by 3 and then added to first equation.

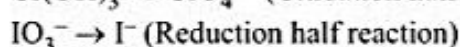
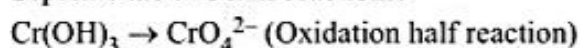


### In alkaline medium

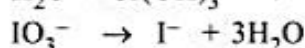
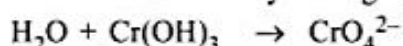
- (a) Consider the reaction



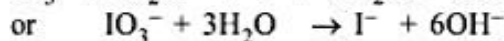
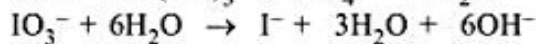
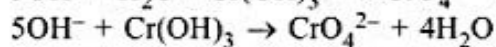
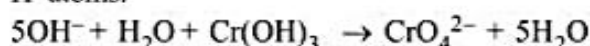
- (b) Separate the two half reactions.



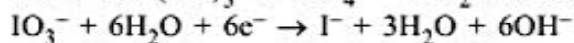
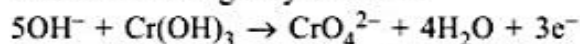
- (c) Balance O- atoms by adding  $H_2O$ .



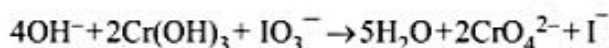
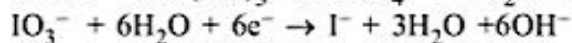
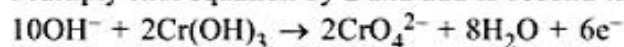
- (d) Balance H-atoms by adding  $H_2O$  to side having deficiency and  $OH^-$  to side having deficiency of H-atoms.



- (e) Balance the charges by electrons

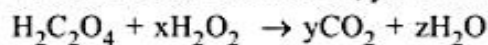


- (f) Multiply first equation by 2 and add to second to give



**Illustration**

1. What will be the value of x, y and z in the following equation –

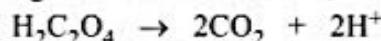


- (A) 2, 1, 2                      (B) 1, 2, 2                      (C) 2, 2, 1                      (D) None

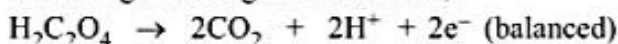
Ans. B

- Sol. (i) The half reaction for oxidation is,  $\text{H}_2\text{C}_2\text{O}_4 \rightarrow \text{CO}_2$   
Balancing carbon atoms on both sides,  $\text{H}_2\text{C}_2\text{O}_4 \rightarrow 2\text{CO}_2$

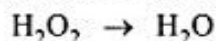
Balancing hydrogen atoms on both sides,



Balancing the charge on both sides,



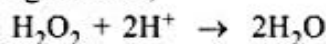
- (ii) The half reaction for reduction is –



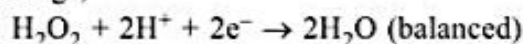
Balancing oxygen atoms on both sides,



Balancing hydrogen atoms,



Balancing the charge,

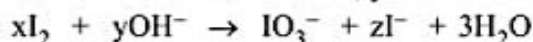


Now, adding both equation,



This is balanced equation.

2. What will be the value of x, y and z in the following equation –



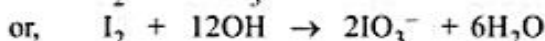
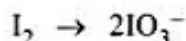
- (A) 3, 5, 6                      (B) 5, 6, 3                      (C) 3, 6, 5                      (D) 6, 3, 5

Ans. C

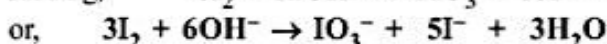
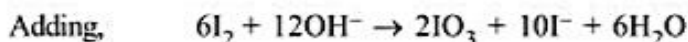
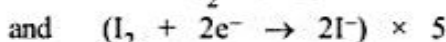
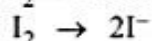
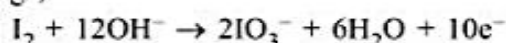
Sol.



Balancing atoms of Iodine on two sides,



Balancing change,



It is balanced equation.

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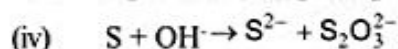
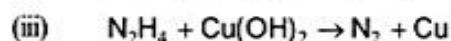
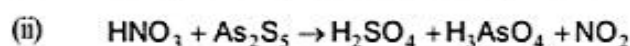
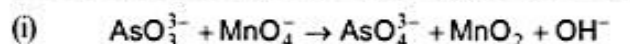
**Exercise**


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1. What will be the value of a, b, c, d, e and f in the following equation –  
 $a\text{MnO}_4^- + b\text{C}_2\text{O}_4^{2-} + c\text{H}^+ \rightarrow d\text{Mn}^{2+} + e\text{CO}_2 + f\text{H}_2\text{O}$   
 (A) 2, 2, 10, 8, 5, 16 (B) 2, 5, 16, 2, 10, 8 (C) 2, 5, 10, 2, 8, 16 (D) 2, 8, 16, 2, 5, 10

Ans. B

2. Balance the following equations using basic medium:



- Ans. (i)  $3\text{AsO}_3^{3-} + 2\text{MnO}_4^- + \text{H}_2\text{O} \rightarrow 3\text{AsO}_4^{3-} + 2\text{MnO}_2 + 2\text{OH}^-$   
 (ii)  $40\text{HNO}_3 + \text{As}_2\text{S}_5 \rightarrow 5\text{H}_2\text{SO}_4 + 2\text{H}_3\text{AsO}_4 + 40\text{NO}_2 + 12\text{H}_2\text{O}$   
 (iii)  $\text{N}_2\text{H}_4 + 2\text{Cu}(\text{OH})_2 \rightarrow \text{N}_2 + 2\text{Cu} + 4\text{H}_2\text{O}$   
 (iv)  $4\text{S} + 6\text{OH}^- \rightarrow 2\text{S}^{2-} + \text{S}_2\text{O}_3^{2-} + 3\text{H}_2\text{O}$   
 (v)  $\text{S}_2\text{O}_4^{2-} + \text{Ag}_2\text{O} + 2\text{OH}^- \rightarrow 2\text{Ag} + 2\text{SO}_3^{2-} + \text{H}_2\text{O}$
- 

## EQUIVALENT WEIGHT

Equivalent weight is primarily used in analytical chemistry because weighing errors are reduced. It is generally determined through the experiments. Equivalent weight is defined in various ways, depending upon the purpose of use.

- (a) The equivalent weight of an element is that weight of the element that will combine with or replace directly or indirectly 1.0 gm of H, 35.5 gm of Cl or 8.0 gm. of O or 108 gm of Ag.  
 (b) In the reaction



1 atom of Mg loses 2 electrons to become  $\text{Mg}^{2+}$  ion. If we start with 1 mole or 24 gm of Mg, we have  $N_A$  ( $6.023 \times 10^{23}$ ) number of Mg atoms which would lose  $2N_A$  number of electrons and form  $N_A$  number of  $\text{Mg}^{2+}$  ions. Therefore, we get  $2N_A$  number of electrons from 24 gm of Mg.

So,  $N_A$  number of electrons can be obtained from  $\frac{24}{2} = 12$  gm of Mg. Thus the equivalent weight of Mg = 12.

Thus equivalent weight of an element is that weight of the element which loses or gained Avogadro number ( $N_A$ ) of electrons.

- (c) Equivalent weight of an element can also be calculating with the help of n factor or valency factor

$$\text{Equivalent weight of element} = \frac{\text{Atomic wt of the element}}{\text{n factor / Valency factor}}$$

$$\text{Equivalent weight of compound} = \frac{\text{Formula wt of the compound}}{\text{n factor / Valency factor}}$$

**n-Factor (n.f.) or Valency factor (v.f.) Calculation :** The above use n-factor is defined for different cases as below :

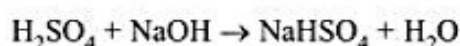
**(A) Acids**

Acids are the species which furnish  $\text{H}^+$  ions when dissolved in a solvent. For acids, n-factor is defined as the number of  $\text{H}^+$  ions replaced by 1 mole of acid in a reaction. The n-factor for acids is not equal to its basicity; i.e. the number of moles of replaceable  $\text{H}^+$  atoms present in one mole of acid.

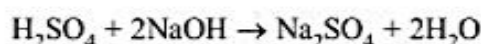
For example, n-factor of  $\text{HCl} = 1$ ,

n-factor of  $\text{HNO}_3 = 1$ ,

n-factor of  $\text{H}_2\text{SO}_4 = 1$  or 2, depending upon extent of reaction it undergoes.



Although one mole of  $\text{H}_2\text{SO}_4$  has 2 replaceable H atoms but in this reaction  $\text{H}_2\text{SO}_4$  has given only one  $\text{H}^+$  ions, so its n-factor would be 1.



The n-factor of  $\text{H}_2\text{SO}_4$  in this reaction would be 2.

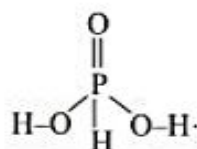
Similarly, n-factor of  $\text{H}_2\text{SO}_4 = 1$  or 2

n-factor of  $\text{H}_2\text{CO}_3 = 1$  or 2

n-factor of  $\text{H}_3\text{PO}_4 = 1$  or 2 or 3

n-factor of  $\text{H}_3\text{PO}_3 = 1$  or 2 because one of the H is not replaceable in  $\text{H}_3\text{PO}_3$ .

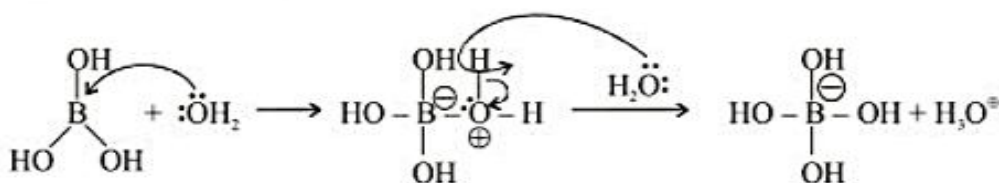
This can be seen using its structure



The H atoms which are linked to oxygen are replaceable while the H atom linked directly to central atom (P) is non replaceable.

n-factor of  $\text{H}_3\text{BO}_3 = 1$

In  $\text{H}_3\text{BO}_3$ , although all three H are linked to oxygen, yet all 3 H are not replaceable. Here, boron atom is electron deficient, so it acts as a Lewis acid. When  $\text{H}_3\text{BO}_3$  is added to water, then oxygen atom of  $\text{H}_2\text{O}$  through its lone pair attack the boron atom, as follows





The net reaction is  $\text{H}_3\text{BO}_3 + 2\text{H}_2\text{O} \rightarrow [\text{B}(\text{OH}_4)]^- + \text{H}_3\text{O}^+$ .

Thus, one mole of  $\text{H}_3\text{BO}_3$  in solution gives only one mole of  $\text{H}^+$ , so its n-factor is 1.

**(B) Bases**

Bases are the species, which furnish  $\text{OH}^-$  ions when dissolved in a solvent. For bases, n-factor is defined as the number of  $\text{OH}^-$  ions replaced by 1 mole of bases in a reaction. The n-factor is not equal to its acidity i.e. the number of moles of replaceable  $\text{OH}^-$  ions present in 1 mole of base.

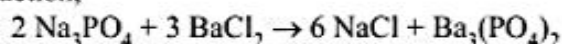
For example,

- n-factor of  $\text{NaOH} = 1$
- n-factor of  $\text{Zn}(\text{OH})_2 = 1$  or 2
- n-factor of  $\text{Ca}(\text{OH})_2 = 1$  or 2
- n-factor of  $\text{Al}(\text{OH})_3 = 1$  or 2 or 3
- n-factor of  $\text{NH}_4(\text{OH}) = 1$

**(C) Salts**

**(i) When no atom undergoes change in oxidation state**

The n-factor for such salts is defined as the total moles of cationic/anionic charge present in 1 mole of the salt. For the reaction,



n-factor of  $\text{Na}_3\text{PO}_4$  in this reaction is 3

n-factor of  $\text{BaCl}_2$  in this reaction is 2

n-factor of  $\text{NaCl}$  in this reaction is 1

n-factor of  $\text{Ba}_3(\text{PO}_4)_2$  in this reaction is 6

**(ii) When only one atom undergoes change in oxidation state and goes in only one product**

The n-factor of such salts is defined as the number of moles of electrons exchanged (lost or gained) by one mole of the salt.

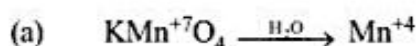
For example, let us calculate the n-factor  $\text{KMnO}_4$  for the given chemical change.



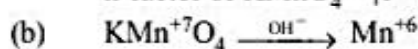
In this reaction, oxidation state of Mn changes from +7 to +2. Thus,  $\text{KMnO}_4$  is acting as oxidising agent, since it is reduced.

$$\therefore \text{n-factor of } \text{KMnO}_4 = |1 \times (+7) - 1 \times (+2)| = 5$$

Similarly



$$\text{n-factor of } \text{KMnO}_4 = |1 \times (+7) - 1 \times (+4)| = 3$$



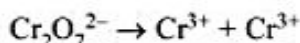
$$\text{n-factor of } \text{KMnO}_4 = |1 \times (+7) - 1 \times (+6)| = 1$$

It can be seen that in all above chemical changes,  $\text{KMnO}_4$  is acting as oxidising agent, yet its n-factor is not same in all reactions. Thus, the n-factor of a compound is not fixed, it depends on the type and the extent of reaction it undergoes.

- (iii) **When only one atom undergoes change in oxidation state but goes in two products with the same oxidation state**

In such case, the n-factor is calculated in the same manner as in case (ii).

For example, let us calculate the n-factor of  $K_2Cr_2O_7$  for the given chemical change.



In this reaction, state of Cr changes from +6 to +3 in both products.

$$\therefore \text{n-factor of } K_2Cr_2O_7 = |2 \times (+6) - 2 \times (+3)| = 6$$

- (iv) **When only one atom undergoes change in oxidation state but goes in two products with different oxidation state**

Consider a chemical change,  $2Mn^{7+} \rightarrow Mn^{4+} + Mn^{2+}$

Out of the two moles of  $Mn^{7+}$ , one mole  $Mn^{7+}$  changes to  $Mn^{4+}$  by gaining 3 moles of electrons and the other mole of  $Mn^{7+}$  changes to  $Mn^{2+}$  by gaining 5 mole of electrons, so in all 8 mole of electrons are gained by 2 mole of  $Mn^{7+}$ . So each mole of  $Mn^{7+}$  has gained  $8/2 = 4$  mole of electrons. Thus, 4 would be the n-factor of  $Mn^{7+}$  in this reaction.

If the reaction would have been



Out of 3 moles of  $Mn^{7+}$ , two moles of  $Mn^{7+}$  changes to  $Mn^{2+}$  by gaining 10 mole of electrons and one mole of  $Mn^{7+}$  changes to  $Mn^{4+}$  by gaining 3 mole of electrons. Thus each mole of  $Mn^{7+}$  have gained  $13/3$  mole of electrons. Therefore, the n-factor of  $Mn^{7+}$  in this reaction would be  $13/3$ .

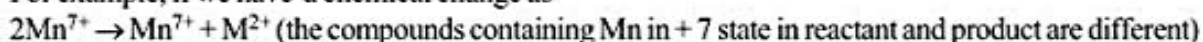
Note that n-factor can be a fraction because it is not the number of electrons exchanged but it is the number of moles of electrons exchanged which can be a fraction.

Now, if the reaction would have been  $3Mn^{7+} \rightarrow Mn^{2+} + 2Mn^{4+}$ . Thus, each mole of  $Mn^{2+}$ . Thus, each mole of  $Mn^{7+}$  have gained  $11/3$  mole of electron. Therefore, n-factor of  $Mn^{7+}$  in this reaction would be  $11/3$ .

**Salts which react in a fashion that only one atom undergoes change in oxidation state but goes in two products with different state (in one product with same oxidation state and in other with different state than in the reactant)**

For such reactions also, the n-factor calculation is not possible without the knowledge of balanced chemical reaction because n-factor of reactant would depend on the fact that how much of reactant underwent change to different oxidation state +y and how much of reactant remained in the same oxidation state +x.

For example, if we have a chemical change as



In this reaction, 5 moles of electrons are gained by 2 moles of  $Mn^{7+}$ , so each mole of  $Mn^{7+}$  takes up  $5/2$  mole of electrons. Therefore, n-factor of  $Mn^{7+}$  in this reaction would be  $5/2$ .



- (v) **When two type of atoms in the salt undergoes change in oxidation state (Both the atoms are either getting oxidised or reduced)**

In this case, the n-factor of the salt will be the total number of mole of electrons lost or gained by one mole of the salt.

For example, for following reaction  $\text{Cu}_2\text{S}^{2-} \rightarrow \text{Cu}^{2+} + \text{S}^{4+}\text{O}_2$

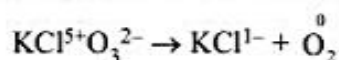
in which  $\text{Cu}^+$  and  $\text{S}^{2-}$  both are getting oxidised to  $\text{Cu}^{2+}$  and  $\text{S}^{4+}$  respectively.

$\therefore$  n-factor of  $\text{Cu}_2\text{S} = (1 \times 2) + (1 \times 6) = 8$

- (vi) **When two atoms in the salt undergoes change in oxidation state (one atom is getting oxidised and the other is getting reduced)**

The n-factor of such a salt can be calculated either by taking the total number of moles of electrons gained by one mole of the salt.

For example, decomposition reaction of  $\text{KClO}_3$  is represented as



In this reaction,  $\text{O}^{2-}$  is getting oxidised to  $\text{O}_2$  and  $\text{Cl}^{5+}$  is getting reduced to  $\text{Cl}^{1-}$ . In each case, 6 mole of electrons are exchanged whether we consider oxidation or reduction

n-factor of  $\text{KClO}_3$  considering oxidation  $= |3(-2) - 3(0)| = 6$

or n-factor of  $\text{KClO}_3$  considering reducing  $= |1 \times (+5) - 1 \times (-1)| = 6$

- (vii) **Salts or compounds which undergoes disproportionation reaction**

Disproportionation reactions can be divided into two types.

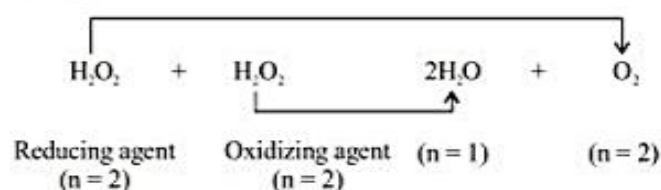
- (a) Disproportionation reactions in which moles of compound getting oxidised and reduced are same i.e. moles of oxidising agent and reducing agent are same. The n-factor for such compounds is calculated by either the number of mole of electrons lost or gained by one mole of the compound because in such a case, n-factor of the compound acting as oxidizing agent or as reducing agent would be same.

For example,  $2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$

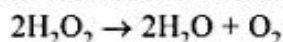
Out of 2 mole of  $\text{H}_2\text{O}_2$  used in reaction, one mole of  $\text{H}_2\text{O}_2$  gets oxidised to  $\text{O}_2$  (oxidation state of O changes from  $-1$  to  $-2$ ). When 1 mole of  $\text{H}_2\text{O}_2$  gets oxidised to  $\text{O}_2$ , the half-reaction would be would be  $\text{O}_2^{2-} \rightarrow \text{O}_2^0 + 2\text{e}^-$

and when 1 mole of  $\text{H}_2\text{O}_2$  gets reduced to  $\text{H}_2\text{O}$ , the half-reaction would be  $\text{O}_2^{2-} + 2\text{e}^- \rightarrow 2\text{O}^{2-}$

Thus, it is evident that one mole of  $\text{H}_2\text{O}_2$  (which is either getting oxidised or reduced) will lose or gain 2 mole of electrons. Therefore, n-factor of  $\text{H}_2\text{O}_2$  as oxidizing as well as reducing agent in this reaction is 2. Thus,

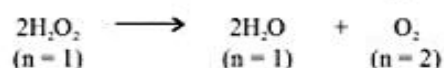


Or when the reaction is written as

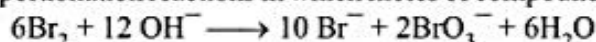


Where,  $\text{H}_2\text{O}_2$  is not distinguished as how much of it functions as oxidizing agent and how much as reducing agent, then n-factor calculation can be done in the following manner. Find the number of electrons exchanged (lost or gained) using the balanced equation and divide it by the number of moles  $\text{H}_2\text{O}_2$  involved in the reaction. Thus, the n-factor of  $\text{H}_2\text{O}_2$  when the reaction is written without segregating

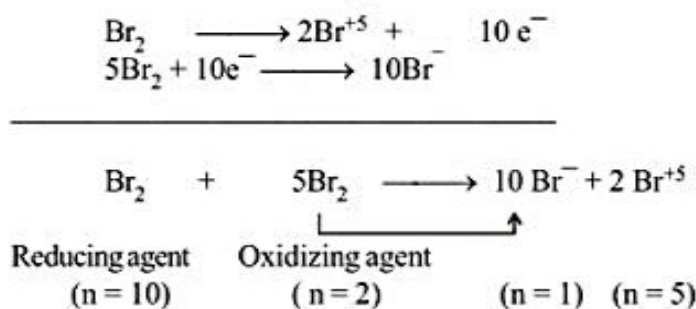
oxidising and reducing agent is  $\frac{2}{2} = 1$



- (b) Disproportionation reactions in which moles of compound getting oxidised and reduced are not same.



In this reaction, the mole of electrons lost by the oxidation of some of the moles of  $\text{Br}_2$  are same as the number of mole of electrons gained by the reduction of rest of the moles of  $\text{Br}_2$ . Of the 6 moles of  $\text{Br}_2$  used, one mole is getting oxidized, losing 10 electrons (as reducing agent) and 5 moles of  $\text{Br}_2$  are getting reduced and accepts 10 moles of electron (as oxidizing agent)

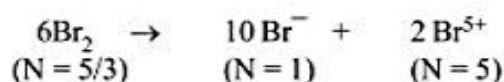


Thus, n-factor of  $\text{Br}_2$  acting as oxidizing agent is 2 and that  $\text{Br}_2$  acting as reducing agent has n-factor 10. Or when the reaction is written as



where,  $\text{Br}_2$  is not distinguished as how much of it function as oxidizing agent and how much as reducing agent, then for calculating n-factor of compound in such reactions, first find the total number of electrons exchanged (lost or gained) using the balanced equation and divide it with the number of mole of  $\text{Br}_2$  involved in the reaction to get the number of mole electrons exchanged by one mole of  $\text{Br}_2$ .

In the overall reaction, the number of mole of electrons exchanged (lost or gained) is 10 and the moles of  $\text{Br}_2$  used in the reaction are 6. Thus, each mole of  $\text{Br}_2$  has exchanged  $10/6$  or  $5/3$  mole of electrons. Therefore, the n-factor of  $\text{Br}_2$  when the reaction is written without segregation oxidising and reducing agent is  $5/3$ .





**Illustration**

1. In acting as a reducing agent, a piece of metal M weighing 16 grams gives up  $2.25 \times 10^{23}$  electrons, what is the equivalent weight of the metal  
 (A) 42.83 (B) 21.33 (C) 83.32 (D) 32

Ans. A

Sol.  $N_A$  no of electron will be removed by

$$\frac{6.023 \times 10^{23}}{2.25 \times 10^{23}} \times 16 \text{ gm of metal M}$$

$$= 42.83 \text{ gm of metal M}$$

$\therefore$  equivalent wt. of metal is 42.83

2. The equiv. wt. of the salt  $\text{KHC}_2\text{O}_4, \text{H}_2\text{C}_2\text{O}_4, 4\text{H}_2\text{O}$  (to be used as a reducing agent) is -

(A)  $\frac{\text{Mol. wt}}{1}$

(B)  $\frac{\text{Mol. wt}}{2}$

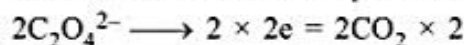
(C)  $\frac{\text{Mol. wt}}{3}$

(D)  $\frac{\text{Mol. wt}}{4}$

Ans. D

Sol. Per mole of this salt contains 2 moles of  $\text{C}_2\text{O}_4^{2-}$

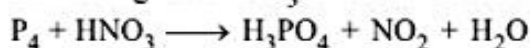
$\therefore$  no of electrons transferred per moles of this salt is



$\therefore$  'n' factor (as a reducing) of the given salt = 4

$$\therefore \text{equiv. wt. of the given salt} = \frac{\text{Mol. wt}}{4}$$

3. What weight of  $\text{HNO}_3$  is needed to convert 62 gm of  $\text{P}_4$  in  $\text{H}_3\text{PO}_4$  in the reaction ?



(A) 63 gm

(B) 630 gm

(C) 315 gm

(D) 126 gm

Ans. B

Sol. The equiv. wt. of  $\text{P}_4 = \frac{31 \times 4}{5 \times 4} = \frac{31}{5}$

$$\therefore 62 \text{ gm } \text{P}_4 = \frac{62 \times 5}{31} \text{ equiv. of } \text{P}_4$$

$$= 10 \text{ equiv. of } \text{P}_4$$

$$\text{The equiv. wt. of } \text{HNO}_3 = \frac{\text{Mol. wt}}{1} = \frac{63}{1}$$

$\therefore$  the wt. of  $\text{HNO}_3$  required

$$= 10 \times 63 = 630 \text{ gm}$$

4. Calculate the n-factor of reactants in the given chemical changes.



- Sol.** (a)  $\text{K}_2\text{Cr}_2\text{O}_7 \xrightarrow{\text{H}^+} \text{Cr}^{3+}$   
 The oxidation state of Cr changes from +6 to +3  
 $\therefore n = |2 \times (+6) - 2 \times (+3)| = 6$
- (b)  $\text{C}_2\text{O}_4^{2-} \rightarrow \text{CO}_2$   
 Carbon get oxidized from +3 to +4  
 $\therefore n = |2 \times (+3) - 2 \times (+4)| = 2$
- (c)  $\text{S}_2\text{O}_3^{2-} \xrightarrow{\text{alkaline}} \text{SO}_4^{2-}$   
 The oxidation state of sulphur changes from +2 to +6  
 $\therefore n = |2 \times (+2) - 2 \times (+6)| = 8$
- (d)  $\text{I}^- \longrightarrow \text{I}^+\text{Cl}$   
 $\text{I}^-$  get oxidized to  $\text{I}^+$   
 $\therefore n = |1 \times (-1) \times (+1)| = 2$

5.  $\text{H}_3\text{PO}_4 + 3\text{NaOH} = \text{Na}_3\text{PO}_4 + 3\text{H}_2\text{O}$

As per the above mentioned equation what is the equivalent weight of  $\text{H}_3\text{PO}_4$ ?

**Sol.** In the mentioned reaction 3 replacable H atoms present in  $\text{H}_3\text{PO}_4$  are replaced by Na

$\therefore$  the  $n = 3$

$$\therefore \text{equiv. wt of } \text{H}_3\text{PO}_4 = \frac{\text{Mol. wt. of } \text{H}_3\text{PO}_4}{3} = \frac{98}{3} \text{ Ans.}$$

6. On heating  $5 \times 10^{-3}$  equiv. of  $\text{CaCl}_2 \cdot x\text{H}_2\text{O}$ , 0.18 gm. of water is obtained, what is the value of x?

**Sol.** Equiv. wt of  $\text{CaCl}_2 \cdot x\text{H}_2\text{O}$

$$= \frac{111 + 18x}{2} = 55.5 + 9x$$

$$\therefore 5 \times 10^{-3} \text{ equiv of } \text{CaCl}_2 \cdot x\text{H}_2\text{O} \\ = 5 \times 10^{-3} (55.5 + 9x) \text{ gm} \\ \text{of } \text{CaCl}_2 \cdot x\text{H}_2\text{O}.$$

$\therefore$  amount of water obtained

$$= \frac{18x}{111 + 18x} \times 5 \times 10^{-3} (55 + 9x) \\ = 9x \times 5 \times 10^{-3}$$

$$\therefore 9x \times 5 \times 10^{-3} = 0.18$$

$$\text{or } x = \frac{0.18}{9 \times 5} \times 10^3 = 4$$

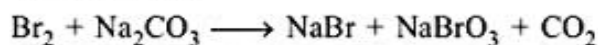
$$\therefore x = 4 \text{ Ans.}$$

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**Exercise**


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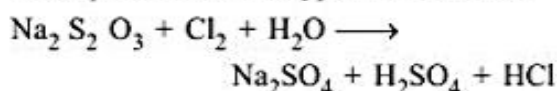
1. In the reaction

The equivalent wt. of  $\text{NaBrO}_3$  is

- (A)  $\frac{\text{Mol. wt}}{1}$                       (B)  $\frac{\text{Mol. wt}}{10}$                       (C)  $\frac{\text{Mol. wt}}{5}$                       (D)  $\frac{\text{Mol. wt}}{4}$

Ans. C

2. The equivalent wt. of hypo in the reaction



is –

- (A)  $\frac{\text{Mol. wt}}{2}$                       (B)  $\frac{\text{Mol. wt}}{4}$                       (C)  $\frac{\text{Mol. wt}}{1}$                       (D)  $\frac{\text{Mol. wt}}{8}$

Ans. D

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**LAW OF EQUIVALENCE**


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The law states that one equivalent of an element combine with one equivalent of the other, and in a chemical reaction equivalent and mill equivalent of reactants react in equal to give same no. equivalent or milli equivalent of products separately.

- (i)
- $a\text{A} + b\text{B} \rightarrow m\text{M} + n\text{N}$

$$m.\text{eq of A} = m.\text{eq. of B} = m.\text{eq of M} = m.\text{eq. of N}$$

- (ii) In a compound
- $\text{M}_x\text{N}_y$

$$m.\text{eq of M}_x\text{N}_y = m.\text{eq of M} = m.\text{eq of N}$$

---

**Illustration**


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1. The number of moles of oxalate ions oxidized by one mole of
- $\text{MnO}_4^-$
- ion in acidic medium.

- (A)  $\frac{5}{2}$                       (B)  $\frac{2}{5}$                       (C)  $\frac{3}{5}$                       (D)  $\frac{5}{3}$

Ans. (A)

Sol. Equivalents of  $\text{C}_2\text{O}_4^{2-} = \text{equivalents of MnO}_4^-$   
 $x (\text{mole}) \times 2 = 1 \times 5$

$$x = \frac{5}{2}$$


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**Exercise**


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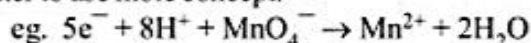
1. What volume of 6 M HCl and 2 M HCl should be mixed to get litre of 3M HCl?

Ans. 1.5 L

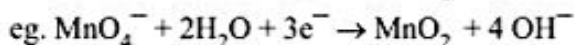
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**Drawbacks of Equivalent concept :**

1. Since equivalent weight of a substance for example oxidising or reducing agent may be variable hence it is better to use mole concept.



$$\therefore \text{Eq. wt of } \text{MnO}_4^- = \frac{\text{MnO}_4^- (\text{Mol.wt.})}{5}$$



$$\therefore \text{Eq. wt. } \text{MnO}_4^- = \frac{\text{MnO}_4^-}{3}$$

Thus the no. of equivalents of  $\text{MnO}_4^-$  will be different in the above two cases but no. of moles will be same.

2. Normality of any solution depends on reaction while molarity does not.

For example

Consider 0.1 mol  $\text{KMnO}_4$  dissolved in water to make 1L solution. Molarity of this solution is 0.1 M. However, its normality is not fixed. It will depend upon the reaction in which  $\text{KMnO}_4$  participates, e.g. If  $\text{KMnO}_4$  forms  $\text{Mn}^{2+}$ , normality =  $0.1 \times 5 = 0.5 \text{ N}$ . This same sample of  $\text{KMnO}_4$ , if employed in a reaction giving  $\text{MnO}_2$  as product (Mn in +4 state) will have normality  $0.1 \times 3 = 0.3 \text{ N}$ .

**ELECTROCHEMICAL CELL**

An electrochemical cell is a system consisting of electrodes that dip into an electrolyte and in which a chemical reaction either uses or generates an electric current.

A voltaic or galvanic cell is an electrochemical cell in which a spontaneous reaction generates an electric current.

A voltaic cell consists of two half-cells that are electrically connected. Each half cell is the portion of an electrochemical cell in which a half-reaction take place.

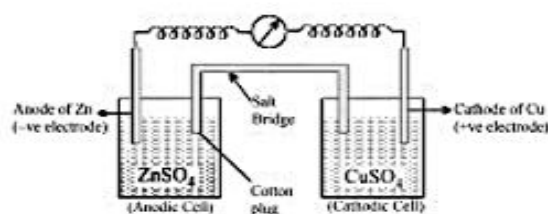
A simple half-cell can be made from a metal strip that dips into a solution of its metal ion. An example is the zinc-zinc ion half-cell (often called simply a zinc electrode), which consists of a zinc metal strip dipping into a solution of a zinc salt. Another simple half-cell consists of a copper metal strip dipping into a solution of a copper salt (copper electrode).

In a voltaic cell, two half-cells are connected in such a way that electrons flow from one metal electrode to another through an external circuit, and ions flow from one half-cell to another through an internal cell connection. Figure given below illustrates an atomic view of a voltaic cell consisting of a zinc electrode and a copper electrode. As long as there is an external circuit, electrons can flow through it from one electrode to another. Because zinc tends to lose electrons more readily than copper, zinc atoms in the zinc electrode lose electrons to produce zinc ions. These electrons flow through the external circuit to the copper electrode, where they react with the copper ions to produce copper metal, and an electric current flows through the external circuit.

The two half-cells must be connected internally to allow ions to flow between them. As zinc ions continue to be produced, the zinc ion solution begins to build up a positive charge. Similarly, as copper ions plate out as copper, the solution builds up a negative charge. The half cell reactions



will stop unless positive ions can move from the zinc half-cell to the copper half cell, and negative ions from the copper half-cell can move to the zinc half-cell. It is necessary that these ion flow occur without mixing of the zinc ion and copper ion solutions. If copper ion come in contact with the zinc metal, for example, direct reaction would occur without an electric current being generated. The voltage would drop, and the battery would run down quickly.



The two half-cells of a voltaic cell are connected by a salt bridge. A salt bridge is a tube of an electrolyte in a gel that is connected to the two half-cells of a voltaic cell; the salt bridge allows the flow of ions but prevents the mixing of the different solutions that would allow direct reaction of the cell reactants. The half-cells are connected externally so that an electric current flows. The two half-cell reactions, as noted earlier, are



The first half-reaction, in which a species loses electrons, is the oxidation half-reaction. The electrode at which oxidation occurs is called the anode. The second half-reaction which a species gains electrons, is the reduction half-reaction. The electrode at which reduction occurs is called the cathode. These definitions of anode and cathode hold for all electrochemical cells, including electrolytic cells.

Sum of the two half-reaction



The net reaction that occurs in the voltaic cell, it is called the cell reaction.

Electrons are given up by the anode (from the oxidation half-reaction) and thus flow from it, whereas electrons are used up by the cathode (by the reduction half-reaction) and so flow into this electrode. The anode in a voltaic cell has a negative sign, because electrons flow from it. The cathode in a voltaic cell has a positive sign.

**Note :** 1. Salt-bridge contains solution of strong ionic salts like NaCl, NaNO<sub>3</sub>, KNO<sub>3</sub>, KCl etc., which is soaked in a colloidal solution of agar-agar gel which permits the movement of ions of salts only.

2. Salt-bridge maintains the electrical neutrality of the solutions in the two half-cells. In the absence of salt bridge, a reverse potential difference is set up in the two half-cells which results in breaking the continuous supply of voltage.

## EMF (ELECTRO MOTIVE FORCE)

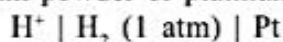
The efficiency of a cell depends on the tendency of anode to lose electrons to cathode and the ability of cathode to receive electrons. Cell efficiency is measured in terms of emf (electromotive force), which is the difference in potentials of two electrodes due to which electrons flow from anode to cathode. EMF value of a cell is constant for given concentration of electrolyte, temperature and the pressure (in case of gases). Therefore, it depends on concentration, temperature and pressure.

EMF of a cell is measured in terms of the difference in electric potential (electrical pressure) between anode and cathode. Its unit is V(volt). The potential of half-cell is known as electrode potential, which is the tendency of an electrode to get oxidized or reduced. Thus, tendency to get oxidized is called oxidation potential and the tendency to get reduced is called reduction potential.

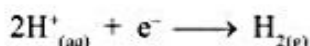
It is not possible to measure the potential of a single electrode; only emf's of cells can be measured. By convention, the reference chosen for comparing electrode potentials is the standard hydrogen electrode.

### Normal or Standard hydrogen electrode (NHE or SHE)

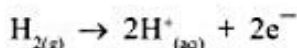
The inert electrode is present in contact with the gas at 1 atm pressure (unless specified) and its ions in the solution. The nature of inert electrode should be such that, when the external voltage is changed even by small amount from the equilibrium value, the reaction will proceed one way or the other. Most suitable electrode is platinum with fine coat of platinum powder or platinum black. It is denoted as :



When reduction occurs at NHE

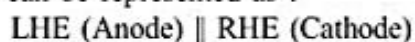


When oxidation occurs at NHE



## CELL NOTATION

A cell can be represented as :



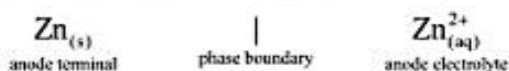
The anode or oxidation half-cell is always written on the left and the cathode or reduction half-cell is written on the right. The two electrodes are electrically connected by means of a salt bridge shown by two vertical bars.



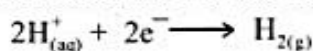


The half-cell which has higher reduction potential, acts as cathode and the electrode with lower reduction potential or higher oxidation potential acts as anode.

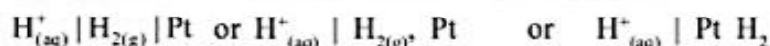
The cell terminals are at the extreme ends in this cell notation, and a single vertical bar indicates a phase boundary - say between a solid terminal and the electrode solution. For the anode of the same cell, you have



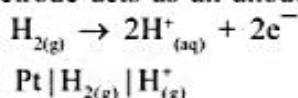
When the half-reaction involves a gas, an inert material such as platinum serves as a terminal and as an electrode surface on which the half-reaction occurs. The platinum catalyzes the half-reaction but otherwise is not involved in it. Hydrogen bubbles over a platinum plate that is immersed in an acidic solution. The cathode half-reaction is



The notation for the hydrogen electrode, written as a cathode, is



when this electrode acts as an anode



Additional examples of electrodes. A comma separates ions present in the same solution.

Cathode	Cathode Reaction
$\text{Cl}_{2(g)}   \text{Cl}^{-}_{(aq)}   \text{Pt}$	$\text{Cl}_{2(aq)} + 2\text{e}^{-} \longrightarrow 2\text{Cl}^{-}_{(aq)}$
$\text{Fe}^{3+}_{(aq)}, \text{Fe}^{2+}_{(aq)}   \text{Pt}$	$\text{Fe}^{3+}_{(aq)} + \text{e}^{-} \longrightarrow \text{Fe}^{2+}_{(aq)}$
$\text{Cd}^{2+}_{(aq)}   \text{Cd}_{(s)}$	$\text{Cd}^{2+}_{(aq)} + 2\text{e}^{-} \longrightarrow \text{Cd}_{(s)}$

## ELECTRO CHEMICAL SERIES

The emf of a voltaic cell depends on the concentrations of substances and the temperature of the cell. For purposes of tabulating electrochemical data, it is usual to choose thermodynamic standard-state conditions for voltaic cells. The standard emf,  $E^{\circ}_{\text{cell}}$ , is the emf of a voltaic cell operating under standard-state conditions (solute concentrations are each 1 M, gas pressures are each 1 atm, and the temperature has a specified value – usually 25°C). Note the superscript degree sign (°), which signifies standard-state conditions.

In this series all species are arranged in decreasing order of their standard reduction potential.

## ELECTRO CHEMICAL SERIES

S.NO.	Reduction half cell reaction	E° in volts at 25°C
1.	$F_2 + 2e^- \longrightarrow 2F^-$	+ 2.65
2.	$S_2O_8^{2-} + 2e^- \longrightarrow 2SO_4^{2-}$	+ 2.01
3.	$Co^{3+} + e^- \longrightarrow Co^{2+}$	+ 1.82
4.	$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \longrightarrow PbSO_4 + 2H_2O$	+ 1.65
5.	$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$	+ 1.52
6.	$Au^{3+} + 3e^- \longrightarrow Au$	+ 1.50
7.	$Cl_2 + 2e^- \longrightarrow 2Cl^-$	+ 1.36
8.	$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$	+ 1.33
9.	$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$	+ 1.229
10.	$Br_2 + 2e^- \longrightarrow 2Br^-$	+ 1.07
11.	$NO_3^- + 4H^+ + 3e^- \longrightarrow NO + 2H_2O$	+ 0.96
12.	$2Hg^{2+} + 2e^- \longrightarrow Hg_2^{2+}$	+ 0.92
13.	$Cu^{2+} + I^- + e^- \longrightarrow CuI$	+ 0.86
14.	$Ag^+ + e^- \longrightarrow Ag$	+ 0.799
15.	$Hg_2^{2+} + 2e^- \longrightarrow 2Hg$	+ 0.79
16.	$Fe^{3+} + e^- \longrightarrow Fe^{2+}$	+ 0.77
17.	$I_2 + 2e^- \longrightarrow 2I^-$	+ 0.535
18.	$Cu^+ + e^- \longrightarrow Cu$	+ 0.53
19.	$Cu^{2+} + 2e^- \longrightarrow Cu$	+ 0.34
20.	$Hg_2Cl_2 + 2e^- \longrightarrow 2Hg + 2Cl^-$	+ 0.27
21.	$AgCl + e^- \longrightarrow Ag + Cl^-$	+ 0.222
22.	$Cu^{2+} + e^- \longrightarrow Cu^+$	+ 0.15
23.	$Sn^{4+} + 2e^- \longrightarrow Sn^{2+}$	+ 0.13
24.	$2H^+ + 2e^- \longrightarrow H_2$	0.00
25.	$Fe^{3+} + 3e^- \longrightarrow Fe$	- 0.036
26.	$Pb^{2+} + 2e^- \longrightarrow Pb$	- 0.126
27.	$Sn^{2+} + 2e^- \longrightarrow Sn$	- 0.14
28.	$AgI + e^- \longrightarrow Ag + I^-$	- 0.151
29.	$Ni^{2+} + 2e^- \longrightarrow Ni$	- 0.25
30.	$Co^{2+} + 2e^- \longrightarrow Co$	- 0.28
31.	$Cd^{2+} + 2e^- \longrightarrow Cd$	- 0.403
32.	$Cr^{3+} + e^- \longrightarrow Cr^{2+}$	- 0.41
33.	$Fe^{2+} + 2e^- \longrightarrow Fe$	- 0.44
34.	$Cr^{3+} + 3e^- \longrightarrow Cr$	- 0.74
35.	$Zn^{2+} + 2e^- \longrightarrow Zn$	- 0.762
36.	$2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$	- 0.828
37.	$Mn^{2+} + 2e^- \longrightarrow Mn$	- 1.18
38.	$Al^{3+} + 3e^- \longrightarrow Al$	- 1.66
39.	$H_2 + 2e^- \longrightarrow 2H^-$	- 2.25
40.	$Mg^{2+} + 2e^- \longrightarrow Mg$	- 2.37
41.	$Na^+ + e^- \longrightarrow Na$	- 2.71
42.	$Ca^{2+} + e^- \longrightarrow Ca$	- 2.87
43.	$Ba^{2+} + 2e^- \longrightarrow Ba$	- 2.90
44.	$Cs^+ + e^- \longrightarrow Cs$	- 2.92
45.	$K^+ + e^- \longrightarrow K$	- 2.93
46.	$Li^+ + e^- \longrightarrow Li$	- 3.03



### Applications of Electrochemical Series :

The important applications of electrochemical series are:

(a) **Strength of Oxidising and Reducing Agents :**

Standard electrode potentials are useful in determining the strengths of oxidizing and reducing agents under standard-state conditions.

$$\text{Strength of reducing agent} \propto \frac{1}{\text{Standard reduction potential}}$$

Strength of oxidising agent  $\propto$  standard reduction potential

Li is strongest reducing agent and  $F_2$  is strongest oxidising agent.

(b) **Standard EMF of a cell ( $E_{\text{Cell}}^0$ ) :**

$E^0$  = difference in potentials of two half-cells

$E^0 = \{\text{standard oxidation potential of anode} - \text{standard oxidation potential of cathode}\}$

$$E_{\text{cell}}^0 = (E_{\text{oxidation}}^0)_{\text{anode}} - (E_{\text{oxidation}}^0)_{\text{cathode}}$$

OR

$E^0 = \{\text{standard reduction potential of a cathode} - \text{standard reduction potential of anode}\}$

$$E_{\text{cell}}^0 = (E_{\text{reduction}}^0)_{\text{cathode}} - (E_{\text{reduction}}^0)_{\text{anode}}$$

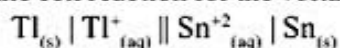
(c) **Predicting feasibility of a redox reaction :** In general, a redox reaction is feasible only if the species which has higher reduction potential is reduced i.e., accepts the electrons and the species which has lower reduction potential is oxidised i.e. loses the electrons. Otherwise, a redox reaction is not feasible. In other words, the species to release electrons must have lesser reduction potential as compared to the species which is to accept electrons.

(d) **To predict whether a metal can liberate hydrogen from acid or not :** only those metals which have negative reduction potentials, can liberate hydrogen from the acids.

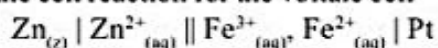
### Illustration

1. Writing the cell Reaction from the Cell Notation

(a) Write the cell reaction for the voltaic cell

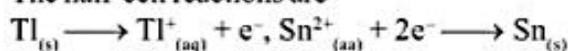


(b) Write the cell reaction for the voltaic cell

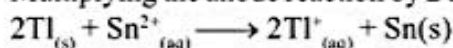


Sol.

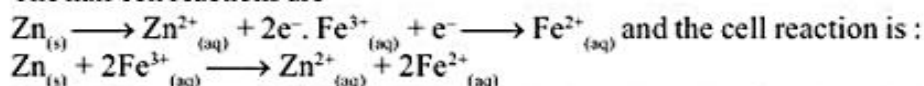
(a) The half-cell reactions are



Multiplying the anode reaction by 2 and then summing the half-cell reactions gives



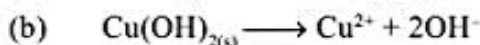
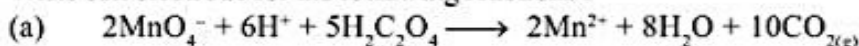
- (b) The half cell reactions are



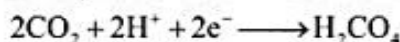
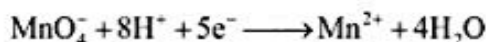
The nature of inert electrode should be such that, when the external voltage is changed even by small amount from the equilibrium value, the reaction will proceed one way or the other. Most suitable electrode is platinum with fine coat of platinum powder or platinum black. **fully specify the voltaic cell, it is necessary to give the concentrations of solutions or ions and the pressure of gases. In the cell notation, these are written within parentheses for each species.**

**For example :**  $\text{Zn}_{(s)} | \text{Zn}^{2+} (1.0 \text{ M}) || \text{H}^+ (1.0 \text{ M}) | \text{H}_2 (1.0 \text{ atm}) | \text{Pt}$

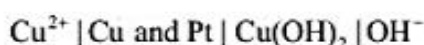
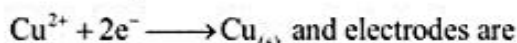
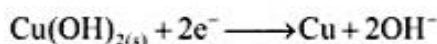
2. Write cell electrode for the following reactions :



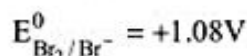
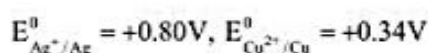
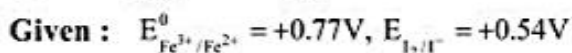
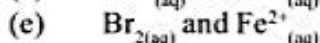
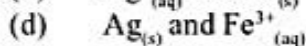
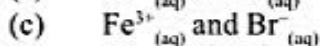
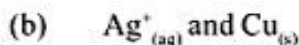
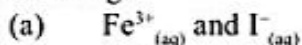
- Sol.**
- (a) Half-cell reactions are



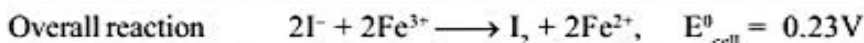
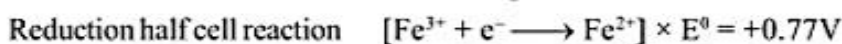
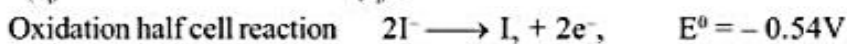
- (b) Half-cell reactions are



3. Using the standard electrode potentials predict the reaction, if any, that occurs between the following:

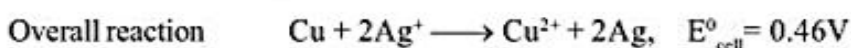
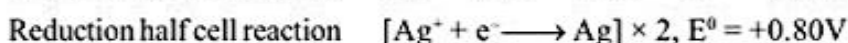
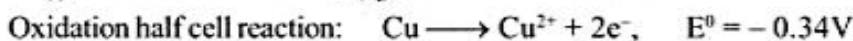


- Sol.**
- (a)
- $\text{I}^-_{(aq)}$
- loses electrons and
- $\text{Fe}^{3+}_{(aq)}$
- gains electrons. Thus



Since  $E^0_{\text{cell}}$  is +ve, the reaction is spontaneous i.e., the reaction does take place.

- (b)
- $\text{Cu}_{(s)}$
- loses electrons and
- $\text{Ag}^+_{(aq)}$
- gains electrons. Thus



Since  $E^0_{\text{cell}}$  is +ve, the reaction is spontaneous

- (c)  $\text{Br}^-_{(\text{aq})}$  loses electrons and  $\text{Fe}^{3+}_{(\text{aq})}$  gains electrons. Thus

Oxidation half cell reaction  $2\text{Br}^- \longrightarrow \text{Br}_2 + 2\text{e}^-$ ,  $E^0 = -1.08\text{V}$

Reduction half cell reaction  $2\text{Fe}^{3+} + 2\text{e}^- \longrightarrow 2\text{Fe}^{2+}$ ,  $E^0 = +0.77\text{V}$

Overall reaction  $2\text{Br}^- + 2\text{Fe}^{3+} \longrightarrow \text{Br}_2 + 2\text{Fe}^{2+}$ ,  $E^0_{\text{cell}} = 0.31\text{V}$

Since  $E^0_{\text{cell}}$  is -ve, the reaction is non-spontaneous, i.e., reaction does not take place.

- (d) Ag loses electrons and  $\text{Fe}^{3+}_{(\text{aq})}$  gains electrons. Thus

Oxidation half cell reaction  $\text{Ag} \longrightarrow \text{Ag}^+ + \text{e}^-$ ,  $E^0 = -0.80\text{V}$

Reduction half cell reaction  $\text{Fe}^{3+} + \text{e}^- \longrightarrow \text{Fe}^{2+}$ ,  $E^0 = +0.77\text{V}$

Overall reaction  $\text{Ag} + \text{Fe}^{3+} \longrightarrow \text{Ag}^+ + \text{Fe}^{2+}$ ,  $E^0_{\text{cell}} = -0.03\text{V}$

Since  $E^0_{\text{cell}}$  is -ve, the reaction is non-spontaneous, i.e., reaction does not take place.

- (e)  $\text{Fe}^{2+}_{(\text{aq})}$  loses electrons and  $\text{Br}_{2(\text{aq})}$  gains electrons. Thus

Oxidation half cell reaction  $2\text{Fe}^{2+} \longrightarrow 2\text{Fe}^{3+} + 2\text{e}^-$ ,  $E^0 = -0.77$

Reduction half cell reaction  $\text{Br}_2 + 2\text{e}^- \longrightarrow 2\text{Br}^-$ ,  $E^0 = +1.08\text{V}$

Overall reaction  $2\text{Fe}^{2+} + \text{Br}_2 \longrightarrow 2\text{Fe}^{3+} + 2\text{Br}^-$ ,  $E^0_{\text{cell}} = +0.31\text{V}$

Since  $E^0_{\text{cell}}$  is +ve, the reaction is spontaneous.

### Exercise

1. Calculate the values for cell

$\text{Zn}_{(\text{s})} | \text{Zn}^{2+}_{(\text{aq})} (1\text{M}) || \text{Cu}^{2+}_{(\text{aq})} (1\text{M}) | \text{Cu}_{(\text{s})}$  (i) cell reaction and (ii) e.m.f. of cell

**Given :**  $E^0_{\text{Cu}^{2+}/\text{Cu}} = +0.35\text{V}$ ;  $E^0_{\text{Zn}^{2+}/\text{Zn}} = -0.76\text{V}$

**Ans.** (i)  $\text{Zn} + \text{Cu}^{2+} \longrightarrow \text{Zn}^{2+} + \text{Cu}$  (ii) 1.11 V

2. Electrode potential of the metals in their respective solution are provided. Arrange the metals in their increasing order of reducing power.

$\text{K}^+/\text{K} = -2.93\text{V}$ ,  $\text{Ag}^+/\text{Ag} = +0.80\text{V}$ ,  $\text{Hg}^+/\text{Hg} = +0.79\text{V}$ ,  $\text{Mg}^{2+}/\text{Mg} = -2.37\text{V}$

$\text{Cr}^{3+}/\text{Cr} = -0.74\text{V}$

**Ans.**  $\text{Ag} < \text{Hg} < \text{Cr} < \text{Mg} < \text{K}$

### REDOX TITRATION

Redox titration is another volumetric technique like neutralization titration, to determine the amount of a specific substance in an unknown sample. This involves oxidation-reduction reaction between the titer and titrant during titration. Oxidation-reduction reaction between ions in the solution can become the basis for the volumetric analysis, provided it fulfills the following conditions.



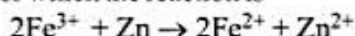
- (1) There is only one reaction under the given condition
- (2) The reaction goes essentially to completion at equivalence point
- (3) A suitable indicator (or other source) is available to locate the end point

The number of reactions fulfilling these conditions is very large. Fortunately, however the general principles involved are common to all and a limited study of only a few reactions is sufficient to give a good understanding of the whole redox analysis. Common methods of redox analysis fall in one of the following three categories :

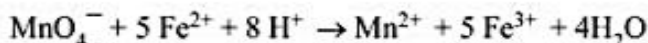
- (i) A solution of substance that is readily oxidized is treated by a standard solution of a strong oxidizing agent. Strong oxidizing agent has good affinity for electron, to ensure the completion of reaction at equivalence point. The most widely used strong oxidizing agents for volumetric analysis are  $\text{MnO}_4^-$  ion in acidic solution,  $\text{Cr}_2\text{O}_7^{2-}$  ion in acidic solution,  $\text{Ce}^{4+}$  ion in acidic solution and  $\text{MnO}_4^-$  in basic solution.

In analysis of reducing agents by titration with a strong oxidizing agent, it is necessary to pre-treat the sample before the titration, to ensure that all the sought substance is reduced to its lower oxidation state and to ensure that no reducing agent other than the sought material is present in the solution.

For example : – The iron sample is dissolved and the solution is treated with a strong reducing agent to convert ferric ion into ferrous ions, if present any. The commonly used reducing agent for this purpose is metallic zinc, for which the reaction is

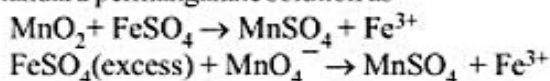


After reduction is complete, the metallic zinc is removed from the solution, which is then titrated by a standard solution of  $\text{KMnO}_4$  as

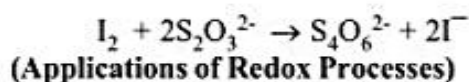


- (ii) If the test sample consists of a strong oxidizing agent, it may be analyzed by titration its solution with a solution of strong reducing agent. The reducing agents commonly used for this purpose are oxalate ion, ferrous ion, arsenious acid etc.

Sample of oxidizing agents that are not fairly soluble in water may be analyzed by treating a known weight of the sample with a measured volume of a standard reducing agent and after the reaction is complete, back titrating the excess of reducing agent in the solution with a standard solution of oxidizing agent. A common analysis of this type is determination of  $\text{MnO}_2$  in a sample pyrolusite. A weighed portion of pyrolusite is treated with a measured volume of  $\text{FeSO}_4$  and excess of  $\text{FeSO}_4$  is then back titrated with a standard permanganate solution as



- (iii) Indirect method : Indirect titration is frequently used for the analysis of oxidizing agents. The sample is treated with a solution of KI, and the liberated iodine is titrated by a solution of sodium thiosulphate " $\text{Na}_2\text{S}_2\text{O}_3$ " (hypo solution), which reacts with iodine as





Titration based on redox processes are called redox titrations. In these titrations titrate/titrant are oxidising/reducing agents. The calculations made in redox titrations are again based on law of chemical equivalence.



Meq. of titrate = meq. of titrant (at equivalent point),

$$\text{or } N_1 V_1 = N_2 V_2$$

Common oxidising agents which are used in redox titration are given below :

1. Acidified  $\text{KMnO}_4$
2. Acidified  $\text{K}_2\text{Cr}_2\text{O}_7$
3. Acidified  $\text{KIO}_3$  and  $\text{KBrO}_3$
4. Acidified  $\text{Ce}^{4+}$  salts
5. Iodine/Iodide (iodimetry and iodometry) etc.

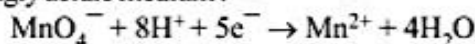
Common oxidising agents used for the preparation of standard solutions

Reagent	Usual conditions for use	Half-reaction	Stability of solution
Potassium permanganate ( $\text{KMnO}_4$ )	Strong acid Weakly acid or neutral strongly basic	$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightleftharpoons \text{Mn}^{2+} + 4\text{H}_2\text{O}$ $\text{MnO}_4^- + 4\text{H}^+ + 3\text{e}^- \rightleftharpoons \text{MnO}_2 + 2\text{H}_2\text{O}$ $\text{MnO}_4^- + \text{e}^- \rightleftharpoons \text{MnO}_4^{2-}$	Solution require Occasional standardization
Quadrivalent cerium ( $\text{Ce}^{4+}$ )	$\text{H}_2\text{SO}_4$ solution	$\text{Ce}^{4+} + \text{e}^- \rightleftharpoons \text{Ce}^{3+}$	Indefinitely stable
Potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ )	Acid solution	$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightleftharpoons 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	Indefinitely stable
Potassium iodate ( $\text{KIO}_3$ )	Strong $\text{HCl}$ solution	$\text{IO}_3^- + 2\text{Cl}^- + 6\text{H}^+ + 4\text{e}^- \rightleftharpoons \text{ICl}_2^- + 3\text{H}_2\text{O}$	Stable
Potassium bromate ( $\text{KBrO}_3 + \text{KBr}$ )	Dilute acid solution	$\text{BrO}_3^- + 5\text{Br}^- + 6\text{H}^+ \rightleftharpoons 3\text{Br}_2 + 3\text{H}_2\text{O}$ $\text{Br}_2 + 2\text{e}^- \rightleftharpoons 2\text{Br}^-$	Indefinitely stable
Iodine ( $\text{I}_2$ )	Neutral, dilute acid or base solution	$\text{I}_2 + 2\text{e}^- \rightleftharpoons 2\text{I}^-$	Restandardisation necessary

### 1. Titration using acidified $\text{KMnO}_4$

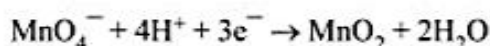
Use of  $\text{KMnO}_4$  as oxidising agent in redox titrations was first made by **F. Marguerette** for the titration of  $\text{Fe}^{2+}$  ions. It is a powerful oxidant and probably the most widely used of all volumetric oxidising agents. It is readily available and colour of its solution is too intense that an indicator is not ordinarily required and  $\text{MnO}_4^-$  ions act as self indicator. Titrations of  $\text{MnO}_4^-$  are usually carried out in acid medium. The possible reactions are :

In strongly acidic medium :



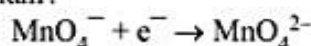
$$E = \frac{M}{5} = \frac{158}{5} = 31.6$$

In weakly acidic or neutral medium :



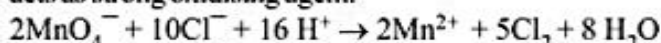
$$E = \frac{M}{3} = \frac{158}{3} = 52.6$$

In alkaline medium :



$$E = \frac{M}{1} = 158$$

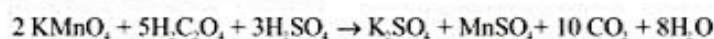
Among the common mineral acids  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$  and  $\text{HNO}_3$  only  $\text{H}_2\text{SO}_4$  is useful for providing acidic medium.  $\text{HCl}$  cannot be used since  $\text{Cl}^-$  are oxidised to  $\text{Cl}_2$  by  $\text{KMnO}_4$ . On the other hand  $\text{HNO}_3$  itself acts as strong oxidising agent.



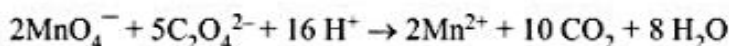
Yet  $\text{KMnO}_4$  fulfils almost all the requirements of a good volumetric oxidising agent but it has some limitation also. The multiplicity of possible reactions at a time, cause uncertainty regarding the stoichiometry of a permanganate oxidation. Also permanganate solution have limited stability and need occasional stabilisation.

Some important titrations using  $\text{K}_2\text{Cr}_2\text{O}_7$  are given below :

**(a)  $\text{KMnO}_4$  vs. oxalic acid :**



Titrant      Titrate  
 oxidising    reducing  
 agent        agent



Reaction is slow initially and needs elevated temperature but after sometime  $\text{Mn}^{2+}$  (Product) catalyse the reaction. (Autocatalysis)

**Medium :** acidic (by  $\text{H}_2\text{SO}_4$ ).

**End point :** Light pink colour of  $\text{MnO}_4^-$  solution,  $\text{KMnO}_4$  acts as self indicator.

**At equivalence point :**

(i) 2 m-mol  $\text{KMnO}_4$  reacts with 5 m-mol oxalic acid.

(ii) meq. of  $\text{KMnO}_4$  = meq. of oxalic acid

$$N_{\text{KMnO}_4} \times V_{\text{KMnO}_4} = N_{\text{oxalic acid}} \times V_{\text{oxalic acid}}$$

$$(iii) \quad \frac{1}{2} \times M_{\text{KMnO}_4} \times V_{\text{KMnO}_4} = \frac{1}{5} \times M_{\text{oxalic acid}} \times V_{\text{Oxalic acid}}$$

**(b)  $\text{KMnO}_4$  vs.  $\text{Fe}^{2+}$  ions :**

$\text{Fe}^{2+}$  is readily oxidised by  $\text{MnO}_4^-$  to  $\text{Fe}^{3+}$ . The reaction which takes place is given below :



**Reducing agent and oxidising agent**

In the laboratory, for practical purposes ferrous ammonium sulphate is taken as a source of  $\text{Fe}^{2+}$  ions. In the determination of Fe content in iron ores, the whole iron content present in a definite amount of its solution is first converted into  $\text{Fe}^{2+}$  by using suitable reducing agent like  $\text{SnCl}_2$ .

**End point :**  $\text{MnO}_4^-$  acts as self indicator and light pink colour of solution indicates end point.

**At equivalent point :**

(i) 1 mol  $\text{MnO}_4^-$  reacts with 5 mol  $\text{Fe}^{2+}$ .

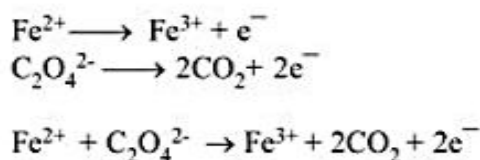
(ii) Meq. of  $\text{MnO}_4^-$  = Meq. of  $\text{Fe}^{2+}$

or 
$$N_{\text{KMnO}_4} \times V_{\text{KMnO}_4} = N_{\text{Fe}^{2+}} \times V_{\text{Fe}^{2+}}$$

$$\text{or } 5 \times M_{\text{KMnO}_4} \times V_{\text{KMnO}_4} = M_{\text{Fe}^{2+}} \times V_{\text{Fe}^{2+}}$$

$$(\because N_{\text{KMnO}_4} = 5 \times M_{\text{KMnO}_4}, N_{\text{Fe}^{2+}} = M_{\text{Fe}^{2+}})$$

**Note :** If titration is being carried out with solution of ferrous oxalate then



$$\text{so } E_{\text{Fe-oxalate}} = \frac{M}{3} \quad (E = \text{Equivalent mass})$$

**(c) Estimation of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions in a solution :**

In this estimation, the solution is titrated twice. First without reduction in which only  $\text{Fe}^{2+}$  reacts and  $\text{Fe}^{3+}$  remains unreacted. In second step same volume of solution is taken.  $\text{Fe}^{3+}$  ions are reduced to  $\text{Fe}^{2+}$  and then then titrated. Here

- (i) In I step : Meq. of  $\text{KMnO}_4$  (let  $x$ ) = Meq. of  $\text{Fe}^{2+}$
- (ii) In II step : Meq.  $\text{KMnO}_4$  ( $y$ ) = Meq. of  $\text{Fe}^{2+}$  + Meq. of  $\text{Fe}^{3+}$   
and Meq. of  $\text{Fe}^{3+}$  ( $y-x$ )

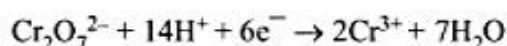
**(d) Analysis of sample containing oxalic acid and sodium oxalate :**

Same volume of solution are titrated separately with  $\text{NaOH}$  and  $\text{KMnO}_4$  solution

$$\begin{aligned}\text{Meq. of NaOH} &= \text{Meq. of oxalic acid} \\ \text{and Meq. of KMnO}_4 &= \text{Meq. of oxalic acid} + \text{Meq. of sodium oxalate}\end{aligned}$$

**2. Titration using acidified  $\text{K}_2\text{Cr}_2\text{O}_7$  :**

In volumetric analysis  $\text{Cr}_2\text{O}_7^{2-}$  is also used commonly as oxidant yet weaker than  $\text{MnO}_4^-$ ,  $\text{Ce}^{4+}$  etc. In most of its applications, it is reduced to  $\text{Cr}^{3+}$ .



$$E_{\text{Cr}_2\text{O}_7^{2-}} = \frac{M_{\text{Cr}_2\text{O}_7^{2-}}}{6} = \frac{296}{6} = 49$$

These titrations are made in 1–2 N acid solution. In neutral or alkaline medium, it is not used. In alkaline medium orange  $\text{Cr}_2\text{O}_7^{2-}$  changes to yellow  $\text{CrO}_4^{2-}$ .

**3. Iodometry and Iodimetry**

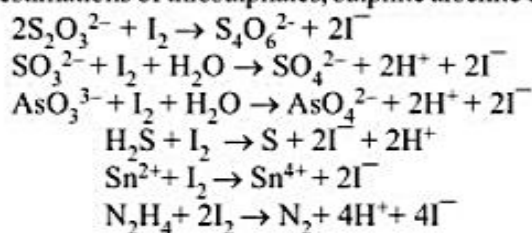
Iodine acts as mild oxidising agent and is used for titrating several analysis. The titrations are based, upon following half reaction



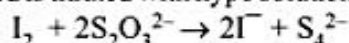


These titrations fall into two categories :

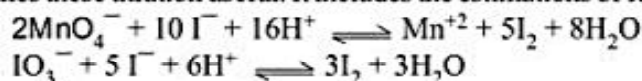
- (a) **Iodimetry** : In these titrations, standard  $I_2$  solution is used to titrate easily oxidisable substances. It includes the estimations of thiosulphates, sulphite, arsenite etc.



- (b) **Iodometry** : In iodometric titrations an oxidising agent is allowed to react with excess of KI (or  $I^-$ ) solution. The  $I_2$  liberated is titrated with hypo solution.

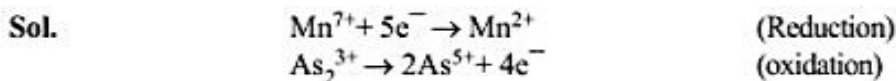


$I_2$  finds use for selective determination of strong reducing agents. Availability of a sensitive and reversible indicator for iodine makes these titration useful. It includes the estimations of following species



### Illustration

1.  $KMnO_4$  solution is to be standardised by titration against  $As_2O_3(s)$ . A 0.1097 g sample of  $As_2O_3$  requires 26.10 ml of the  $KMnO_4$  solution for its titration. What are the molarity and normality of the  $KMnO_4$  solution?



$$\therefore \text{Meq. of } As_2O_3 = \text{meq of } KMnO_4$$

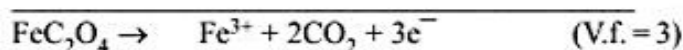
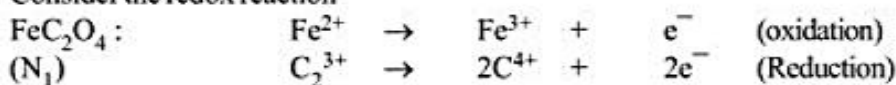
$$\frac{0.1097}{198} \times 1000 = 26.10 \times N \quad (E_{As_2O_3} = M/4)$$

$$\therefore N_{KMnO_4} = 0.085$$

$$\therefore M_{KMnO_4} = \frac{0.085}{5} = 0.017$$

2. 100 ml solution of  $FeC_2O_4$  and  $FeSO_4$  is completely oxidized by 60 ml of 0.02 M  $KMnO_4$  in acid medium. The resulting solution is then reduced by Zn and dil. HCl. The reduced solution is again oxidized completely by 40 ml 0.02 M  $KMnO_4$ . Calculate normality of  $FeC_2O_4$  and  $FeSO_4$  in mixture.

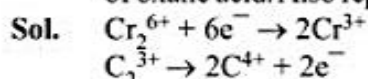
**Sol.** Consider the redox reaction





$$\begin{aligned} 100(N_1 + N_2) &= 60 \times 0.02 \times 5 \\ (N_1 + N_2) &= 3 \times 0.02 \end{aligned} \quad \dots\dots\dots(1)$$

4. What was of  $K_2Cr_2O_7$  is required to produce 5.0 litre  $CO_2$  at  $75^\circ C$  and 1.07 atm pressure from excess of oxalic acid. Also report the volume of 0.1 N NaOH required to neutral the  $CO_2$  evolved.



$$\begin{aligned} \text{meq. of } K_2Cr_2O_7 &= \text{meq. of } CO_2 \text{ formed} \\ &= \text{mole of } CO_2 \times 1000 \times 1 \text{ (V.f for } CO_2 = 1) \\ &= \frac{PV}{RT} \times 1 \times 1000 = \frac{1.07 \times 5 \times 1000}{0.0821 \times 348} = 187.3 \end{aligned}$$

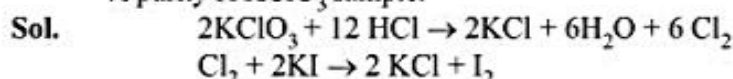
$$\therefore \frac{W_{K_2Cr_2O_7}}{M/6} \times 1000 = 187.3$$

$$\text{or } w_{K_2Cr_2O_7} = \frac{187.3 \times M}{6 \times 1000} = \frac{187.3 \times 294}{6 \times 1000};$$

$$\begin{aligned} w &= 9.18 \text{ g} & (M_{K_2Cr_2O_7} = 294) \\ CO_2 + NaOH &\rightarrow Na_2CO_3 + H_2O & (\text{V.f. for } CO_2 = 2) \end{aligned}$$

$$\begin{aligned} \text{Also meq. of NaOH} &= \text{meq. of } CO_2 \text{ of valence factor 2} \\ 0.1 \times V &= 187.3 \times 2 = 3.746 \text{ L} \end{aligned}$$

5. 2.480 g of  $KClO_3$  are dissolved in conc. HCl and the solution was boiled. Chlorine gas evolved in the reactions was then passed through a solution of KI and liberated iodine was titrated with 100 ml of hypo. 12.3 ml of same hypo solution required 24.6 ml of 0.5 iodine for complete neutralization. Calculate % purity of  $KClO_3$  sample.



$$\begin{aligned} \text{Also meq. of } I_2 &= \text{meq. of hypo} = 100 \times 1 \\ [\because N_{Hypo} \times 12.3 &= 24.6 \times 0.5, \therefore N_{Hypo} = 1] \end{aligned}$$

$$\text{Also mM of } Cl_2 = \text{mM of } I_2 = \frac{100}{2} = 50$$

$$\text{Also mM of } KClO_3 = \frac{2 \times \text{mM of } Cl_2}{6} = \frac{2 \times 50}{6} = \frac{50}{3}$$

$$\therefore \frac{W_{KClO_3}}{122.5} \times 1000 = \frac{50}{3} \quad \Rightarrow \quad W_{KClO_3} = 2.042$$

$$[\text{milli-mole (mM)} = (\text{mass} \times 1000) / (\text{mol. mass})]$$

$$\therefore \% KClO_3 = \frac{2.042}{2.48} \times 100 = 82.34 \%$$



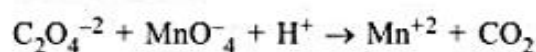
## IMPORTANT VARIATIONS

- (1) Oxidising property  $\propto$  Tendency of accepting electron(s)
- (2) Oxidising property  $\propto$  Electronegativity
- (3) Oxidising property  $\propto \frac{1}{\text{Ionic or atomic size}}$
- (4) Oxidising property  $\propto$  Oxidation number
- (5) Reducing property  $\propto$  Tendency of losing electron(s)
- (6) Reducing property  $\propto$  Ionic or atomic size
- (7) Reducing property  $\propto \frac{1}{\text{Electronegativity}}$
- (8) Reducing property  $\propto \frac{1}{\text{Oxidation number}}$
- (9) Decreasing order of reducing strength of metals  
 $\text{Zn} > \text{Fe} > \text{Pb} > \text{Cu} > \text{Ag}$
- (10) Decreasing order of oxidising strength of metal ion  
 $\text{Ag}^+ > \text{Cu}^{+2} > \text{Pb}^{+2} > \text{Fe}^{+2} > \text{Zn}^{+2}$
- (11) Order of oxidising efficiency  
 $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$
- (12) Order of reducing efficiency  
 $\text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^-$



## SOLVED EXAMPLE

**Q.1** In the reaction

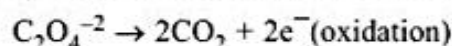


the reductant is –

- (A)  $\text{C}_2\text{O}_4^{-2}$                       (B)  $\text{H}^+$                       (C)  $\text{MnO}_4^-$                       (D) None of the above

**Ans.** (A)

**Sol.** In the above reaction  $\text{C}_2\text{O}_4^{-2}$  acts as a reductant because it is oxidised to  $\text{CO}_2$  as :



$\text{C}_2\text{O}_4^{-2}$  reduces  $\text{MnO}_4^-$  to  $\text{Mn}^{+2}$  ion in solution.

**Q.2** Oxidation number of cobalt in  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_2\text{Br}$  is –

- (A) + 6                      (B) Zero                      (C) + 3                      (D) + 2

**Ans.** (C)

**Sol.** Let the O.N. of Co be x

O.N. of  $\text{NH}_3$  is zero

O.N. of Cl is -1

O.N. of Br is -1

$$\text{Hence, } x + 6(0) - 1 \times 2 - 1 = 0$$

$$\therefore x = +3$$

so, the oxidation number of cobalt in the given complex compound is +3.

**Q.3** Arrange the following in order of

a) Increasing oxidation number:  $\text{MnCl}_2$ ,  $\text{MnO}_2$ ,  $\text{Mn}(\text{OH})_3$ ,  $\text{KMnO}_4$

b) Increasing oxidation number:  $\text{HIO}_4$ ,  $\text{ICl}$ ,  $\text{HI}$ ,  $\text{I}_2$

c) Decreasing oxidation number:  $\text{HXO}_4$ ,  $\text{HXO}$ ,  $\text{HXO}_3$ ,  $\text{HXO}_2$

<b>Sol.</b>	a)	$\text{MnCl}_2$	<	$\text{Mn}(\text{OH})_3$	<	$\text{MnO}_2$	<	$\text{KMnO}_4$
		Ox. no. +2		+3		+4		+7
		$\text{HI}$	<	$\text{I}_2$	<	$\text{ICl}$	<	$\text{HIO}_4$
	b)	Ox. no. +7		+5		+3		+1
		$\text{HXO}_4$	>	$\text{HXO}_3$	>	$\text{HXO}_2$	>	$\text{HXO}$
	c)	Ox. no. -1		0		+1		+7

**Q.4** The composition of a sample of wustite is  $\text{Fe}_{0.93}\text{O}$ . What percentage of iron is present in the form of Fe(III)?

**Sol.** Ox. no. of Fe in wustite =  $\frac{200}{93}$

It is an intermediate value in between the oxidation state of Fe(II) and Fe(III). let percentage of Fe(III) in wustite be x, then

$$2x(100 - x) + (3 \times x) = \frac{200}{93} \times 100 \quad \therefore x = 15.05\%$$

- Q.5** One mole of  $\text{N}_2\text{H}_4$  loses 10 mole electrons to form a new compound Y. Assuming that all the  $\text{N}_2$  appears in new compound, what is the oxidation state of Nitrogen in Y? (There is no change in the oxidation state of H)

**Sol.**  $\text{N}_2\text{H}_4 \rightarrow (\text{Y}) + 10\text{e}^-$   
 ( $\because$  Y contains all N atoms)  
 $\therefore \text{N}_2^{2-} \rightarrow (\text{N})^x + 10\text{e}^-$   
 $-4 = 2x - 10$   
 $x = +3$   
 $\therefore$  oxidation state of N in Y is +3

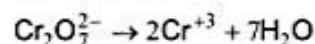
- Q.6** Balance the equation :  
 $\text{Cr}_2\text{O}_7^{2-} + \text{C}_2\text{O}_4^{2-} + \text{H}^+ \rightarrow \text{Cr}^{+3} + \text{CO}_2 + \text{H}_2\text{O}$

**Sol.** Reduction :  $\text{Cr}_2\text{O}_7^{2-} \rightarrow \text{Cr}^{+3}$       Oxidation :  $\text{C}_2\text{O}_4^{2-} \rightarrow \text{CO}_2$

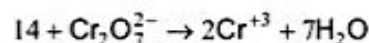
Balancing atoms other than O and H :  $\text{Cr}_2\text{O}_7^{2-} \rightarrow 2\text{Cr}^{+3}$

Reaction is taking place in acidic medium

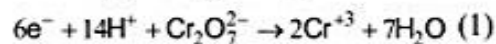
Balancing O



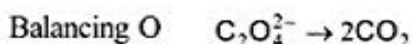
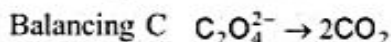
Balancing H



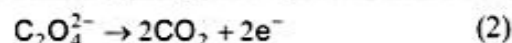
Balancing charges we get reduction half-reaction.



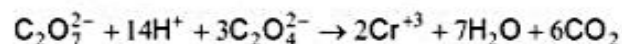
Balancing oxidation reaction:



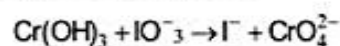
Balancing charges, we get oxidation half-reaction



Multiplying (2) by 3 and adding to (1) (To cancel out the electrons)

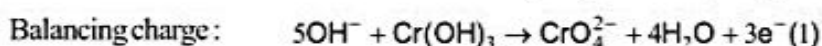
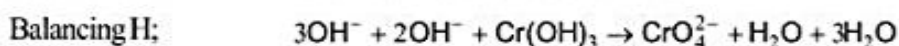
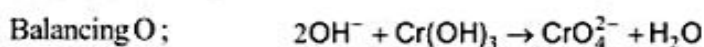
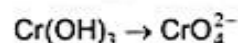


- Q.7** Balance the equation

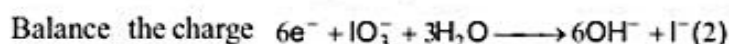
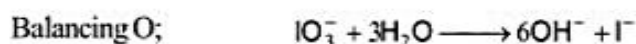


**Sol.** Oxidation :  $\text{Cr}(\text{OH})_3 \rightarrow \text{CrO}_4^{2-}$       Reduction :  $\text{IO}_3^- \rightarrow \text{I}^-$

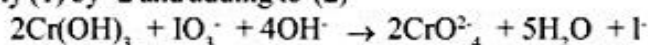
Balancing oxidation reaction: Balancing atoms other than H and O



Balancing reduction reaction:



Multiply (1) by 2 and adding to (2)

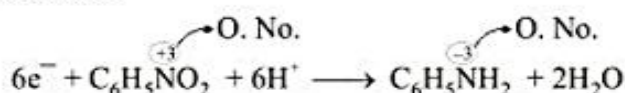


**Q.8** Find the number of electrons released or absorbed to produce 18.6 gm aniline from nitrobenzene in acidic medium is

(A) 1.2 moles released (B) 1.2 moles absorbed (C) 6 moles released (D) 6 moles absorbed

**Ans.** (B)

**Sol.** Balanced reaction

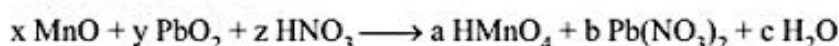


$\therefore$  To produce 93 gm (or 1 mole) aniline absorbed number of moles of electron in above reaction = 6

$\therefore$  To produce 18.6 gm (or 1 mole) aniline absorbed number of moles of electron in above reaction

$$= \frac{6}{93} \times 18.6 \Rightarrow 1.2 \quad \text{Ans.}$$

**Q.9** In the redox reaction:



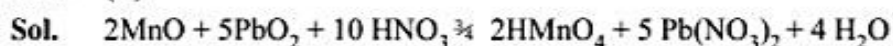
(A)  $x = 2, y = 5, z = 10$

(B)  $x = 2, y = 7, z = 8$

(C)  $x = 2, y = 5, z = 8$

(D)  $x = 2, y = 5, z = 5$

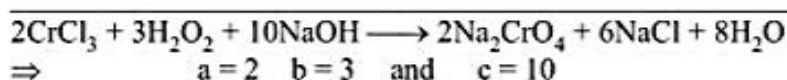
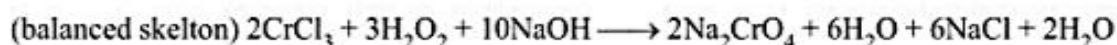
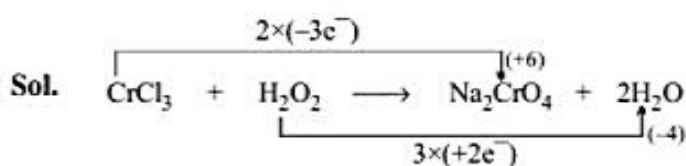
**Ans.** (A)



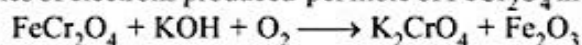
**Q.10** Calculate the sum of stoichiometric coefficients of products in minimum integral balanced following chemical reaction.



**Ans.** 16



**Q.11** Number of moles of electrons produced per mole of  $\text{FeCr}_2\text{O}_4$  in the following redox reaction.



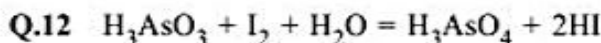
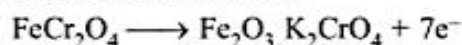
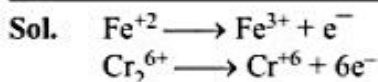
(A) 6

(B) 1

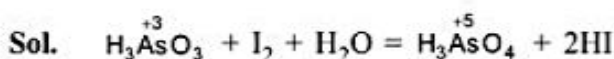
(C) 7

(D) 3

**Ans.** (C)



0.01 equivalent of the mentioned acid will neutralize how many grams of NaOH ?

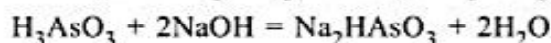


$$\therefore n = 2$$

$$\therefore \text{equiv. wt of } \text{H}_3\text{AsO}_3$$

$$= \frac{\text{Mol. wt. of } \text{H}_3\text{AsO}_3}{2} = \frac{126}{2} = 63$$

$$\therefore 0.01 \text{ equiv of } \text{H}_3\text{AsO}_3 = 0.63 \text{ gm } \text{H}_3\text{AsO}_3$$



126gm  $\text{H}_3\text{AsO}_3$  reacts

with 80 gm. of NaOH

0.63 gm.  $\text{H}_3\text{AsO}_3$  reacts

$$\text{with } \frac{80}{126} \times 0.63 \text{ gm of NaOH}$$

$$= 0.4 \text{ gm of NaOH Ans.}$$

**Q.13** The equivalent weight of a metal is 36. What weight of the metal would give 9.322 gm of its chloride ?

Sol. The equiv. wt. of metal = 36

The equiv. wt. of chlorine = 35.5

Equiv wt of metal chloride = 71.5

71.5 gm. metal chloride contain 36 gm of metal

9.322 gm metal chloride contain

$$\frac{36}{71.5} \times 9.322 \text{ gm of metal}$$

$$= 4.6935 \text{ gm of metal}$$

$$\therefore 4.6935 \text{ gm metal give 9.322 gm metal chloride Ans.}$$

**Q.14** In a reaction vessel, 1.184 g of NaOH is required to be added for completing the reaction. How many millilitre of 0.15 M NaOH should be added for this requirement ?

Sol. Amount of NaOH present in 1000 ml of 0.15 M NaOH =  $0.15 \times 40 = 6 \text{ g}$

$$\therefore 1 \text{ ml of this solution contain NaOH} = \frac{6}{100} \times 10^{-3}$$

$$\therefore 1.184 \text{ g of NaOH will be present in } \frac{1}{6 \times 10^{-3}} \times 1.184 = 197.33 \text{ ml}$$



**Q.15** What weight of  $\text{Na}_2\text{CO}_3$  of 85% purity would be required to prepare 45.6 ml of 0.235 N  $\text{H}_2\text{SO}_4$  ?

**Sol.** Meq. of  $\text{Na}_2\text{CO}_3$  = Meq. of  $\text{H}_2\text{SO}_4$   
 $= 45.6 \times 0.235$

$$\therefore \frac{W_{\text{Na}_2\text{CO}_3}}{E_{\text{Na}_2\text{CO}_3}} \times 1000 = 45.6 \times 0.235$$

$$\Rightarrow \frac{W_{\text{Na}_2\text{CO}_3}}{106/2} \times 1000 = 45.6 \times 0.235$$

$$\therefore W_{\text{Na}_2\text{CO}_3} = 0.5679 \text{ g}$$

For 85 g of pure  $\text{Na}_2\text{CO}_3$ , weighed sample = 100 g

$$\therefore \text{For } 0.5679 \text{ g of pure } \text{Na}_2\text{CO}_3, \text{ weighed sample} = \frac{100}{85} \times 0.5679 = 0.6681 \text{ g}$$

**Q.16** Two solution of 0.1 M  $\text{Cr}_2\text{O}_7^{2-}$  (aq) and 0.1 M  $\text{MnO}_4^-$  (aq) are to be titrate  $\text{Fe}^{2+}$  (aq) separately:  
 (a) With which solution,  $\text{Cr}_2\text{O}_7^{2-}$  (aq) or  $\text{MnO}_4^-$  (aq), would the greater volume of titrant (titrating solution) be required for a given solution of  $\text{Fe}^{2+}$  (aq).  
 (b) If a given titration required 24.50 ml of 0.1 M  $\text{Cr}_2\text{O}_7^{2-}$  (aq), how many ml of 0.100 M  $\text{MnO}_4^-$  (aq) would have been required if it had been used instead ?

**Sol.** Redox changes with  $\text{MnO}_4^-$  and  $\text{Cr}_2\text{O}_7^{2-}$  are :



When solution containing same equivalent of  $\text{Fe}^{2+}$ , are titrated with  $\text{Cr}_2\text{O}_7^{2-}$  and  $\text{MnO}_4^-$  separately, then

$$\begin{array}{l} \text{meq. of } \text{Fe}^{2+} = \text{meq. of } \text{Cr}_2\text{O}_7^{2-} = \text{meq. of } \text{MnO}_4^- \\ \text{meq. of } \text{Fe}^{2+} = 0.1 \times 6 \times V_1 = 0.1 \times 5 \times V_2 \end{array} \quad \dots\dots\dots(1)$$

$$\therefore \frac{V_2 (\text{for } \text{MnO}_4^-)}{V_1 (\text{for } \text{Cr}_2\text{O}_7^{2-})} = \frac{6}{5} = 1.20$$

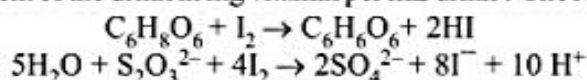
Thus, volume of  $\text{MnO}_4^-$  required will be 1.2 times of volume of  $\text{Cr}_2\text{O}_7^{2-}$ .

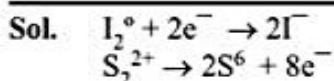
(b) To calculate  $V_{\text{MnO}_4^-}$  needed. Using the given data in eq. (1)

$$24.5 \times 0.1 \times 6 = 0.1 \times 5 \times V_{\text{MnO}_4^-}$$

$$\Rightarrow V_{\text{MnO}_4^-} = 29.4 \text{ ml}$$

**Q.17** A 200 ml sample of a citrus fruit drinks containing ascorbic acid (Vitamin C, mol. wt. 176.13) was acidified with  $\text{H}_2\text{SO}_4$  and 10 ml of 0.0250 M  $\text{I}_2$  was added. Some of the iodine was reduced by the ascorbic acid to  $\text{I}^-$ . The excess of  $\text{I}_2$  required 4.6 ml of 0.01 M  $\text{Na}_2\text{S}_2\text{O}_3$  for reduction. What was the vitamin C content of the drink in mg vitamin per mL drink ? The reactions are :



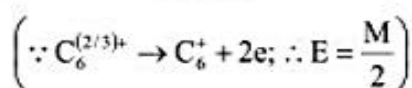


V.f. for  $I_2$  and  $S_2O_3^{2-}$  are 2 and 8 respectively.

Now, meq. of ascorbic acid in 200 mL solution

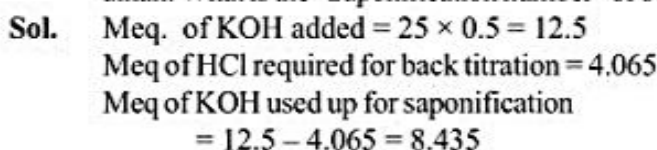
$$\begin{aligned} &= \text{meq. of } I_2 \text{ used by ascorbic acid} \\ &= \text{meq. of } I_2 \text{ added} - \text{meq. of } I_2 \text{ left} \\ &= 0.0250 \times 2 \times 10 - 0.01 \times 8 \times 4.6 \\ &= 0.5 - 0.368 = 0.132 \end{aligned}$$

$$\therefore w = \frac{0.132 \times \text{Eq.mass}}{1000} = \frac{0.132 \times 176.13}{2 \times 1000}$$



$$\therefore = 0.0116 \text{ g/200 ml} = 0.058 \text{ mg/ml}$$

- Q.18** The "saponification number" of a fat or oil is defined as the number of milligram of KOH required to saponify 1.0 g of fat or oil. To a sample of butter weighing 2.0 g is added a 25 ml 0.5 N KOH solution. After saponification is complete, 8.13 ml of 0.5 N HCl is found to be required to neutralize the excess alkali. What is the "Saponification number" of butter?

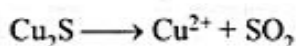
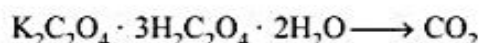


$$\begin{aligned} \text{mg of KOH used for saponification} \\ &= 8.435 \times 56 = 472.36 \end{aligned}$$

$$\text{mg of KOH used for saponification of 1.0 g butter} = 472.36 / 2 = 236.18$$

$$\text{Saponification number} = 236.18$$

- Q.19** Container-I may contain 1 mol  $K_2Cr_2O_7$  or 1 mol  $KMnO_4$  in acidic medium. This container-I is mixed with other container-II, III, IV or V, due to which compound present in these containers undergo following half reaction.



$KMnO_4$ or $K_2Cr_2O_7$	KI	$Cu_2S$	$K_2C_2O_4$ $\cdot 3H_2C_2O_4$ $\cdot 3H_2O$	$NH_4SCN$
Container-I	Container-II	Container-III	Container-IV	Container-V

Column I represents the two container which are mixed.

Column II represents the number of moles of substance which reacts with 1 mol of substance (may be  $KMnO_4$  or  $K_2Cr_2O_7$ ) present in container-I.

Match the column I with Column-II.

Column I	Column II
(A) Container-I + Container-III	(P) $\frac{3}{4}$
(B) Container-II + Container-I	(Q) $\frac{5}{8}$
(C) Container-I + Container-V	(R) 1
(D) Container-IV + Container-I	(S) $\frac{5}{6}$

**Ans.** (A) P,Q; (B) R,S; (C) R,S; (D) P,Q

<b>Sol.</b> (A)	Container-I reacts with container-II n factor of KI = 6 $\text{KMnO}_4$ $1 \times 5 = x \times 6$ $x = \frac{5}{6}$	$\text{K}_2\text{Cr}_2\text{O}_7$ $1 \times 6 = x \times 6$ $x = 1$
(B)	n factor of $\text{Cu}_2\text{S} = 8$ $\text{KMnO}_4$ $1 \times 5 = x \times 8$ $x = \frac{5}{8}$	$\text{K}_2\text{Cr}_2\text{O}_7$ $1 \times 6 = x \times 8$ $x = \frac{6}{8} = \frac{3}{4}$
(C)	n factor of $\text{K}_2\text{C}_2\text{O}_4 \cdot 3\text{H}_2\text{C}_2\text{O}_4 \cdot 3\text{H}_2\text{O} = 8$ $\text{KMnO}_4$ $x = \frac{5}{8}$	$\text{K}_2\text{Cr}_2\text{O}_7$ $x = \frac{3}{4}$
(D)	n factor of $\text{NH}_4\text{SCN} = 6$ $\text{KMnO}_4$ $x = \frac{5}{6}$	$\text{K}_2\text{Cr}_2\text{O}_7$ $x = 1$

**Q.20** 0.1 N  $\text{K}_2\text{C}_2\text{O}_4 \cdot 3\text{H}_2\text{C}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$  solution reacts completely with 20 ml 0.05 M of  $\text{KMnO}_4$  solution in acidic medium. Another sample of same solution of  $\text{K}_2\text{C}_2\text{O}_4 \cdot 3\text{H}_2\text{C}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$ , having same volume is titrated with  $\frac{1}{8}$  M NaOH solution, then volume of NaOH solution is

- (A) 20 ml                      (B) 30 ml                      (C) 50 ml                      (D) None of these

**Ans.** (B)

**Sol.** Redox titration  
Eq. of  $\text{K}_2\text{C}_2\text{O}_4 \cdot 3\text{H}_2\text{C}_2\text{O}_4 \cdot 4\text{H}_2\text{O} = \text{Eq. of } \text{KMnO}_4$   
 $\frac{0.1 \times V}{1000} = \frac{20 \times 0.05 \times 5}{1000}$   
 $V = 50 \text{ ml}$   
n factor of  $\text{K}_2\text{C}_2\text{O}_4 \cdot 3\text{H}_2\text{C}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$   
for redox titration = 8  
for acid base titration = 6

$\therefore$  for acid base titration normality of  $K_2C_2O_4 \cdot 3H_2C_2O_4 \cdot 4H_2O = \frac{0.1}{8} \times 6 N$

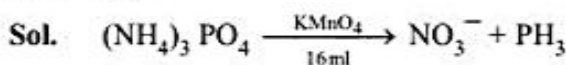
Eq. of acid = Eq. of base

$$\frac{0.1 \times 50}{8 \times 1000} \times 6 = \frac{1}{8} \times \frac{V_{ml}}{1000}$$

$V_{ml} = 30 \text{ ml}$  Ans.

- Q.21**  $(NH_4)_3PO_4$  get converted into  $NO_3^-$  and  $PH_3$  on reacting with  $KMnO_4$  in acidic medium. If 50 ml of 0.2 M  $(NH_4)_3PO_4$  solution reacts with 16 ml of  $KMnO_4$  solution, then normality of  $KMnO_4$  solution is  
(A) 5 (B) 8 (C) 10 (D) 20

**Ans.** (C)



$$50 \times 0.2 \text{ M}$$

n-factor of  $KMnO_4$  in acidic medium = 5

n-factor of  $(NH_4)_3PO_4 = 16$

Eq. of  $(NH_4)_3PO_4 = \text{Eq. of } KMnO_4$

$$\frac{0.2 \times 50}{1000} \times 16 = \frac{N \times 16}{1000}$$

$N = 10$  Ans.

- Q.22** The number of moles of NaOH required to completely react with 20 ml of 0.1 M  $NaH_2PO_3$  solution and 40 ml of 0.1 M  $NaHCO_3$ .

(A)  $8 \times 10^{-3}$  (B)  $2 \times 10^{-3}$  (C)  $4 \times 10^{-3}$  (D)  $6 \times 10^{-3}$

**Ans.** (D)

**Sol.** Eq. of  $NaH_2PO_3 + \text{Eq. of } NaHCO_3 = \text{Eq. of } NaOH$

$$\frac{20 \times 0.1}{1000} \times 1 + \frac{40 \times 0.1}{1000} \times 1 = x$$

$x = 6 \times 10^{-3}$  Ans.]

- Q.23** 70 ml of a solution containing HCl was treated with excess of  $KBrO_3$  and KBr solution of unknown concentration where  $Br_2$  liberated is titrated against a standard solution of 21 ml of 2M  $Na_2S_2O_3$  solution. Molarity of HCl solution is

(A)  $\frac{2}{10}$  (B)  $\frac{36}{100}$  (C)  $\frac{6}{10}$  (D)  $\frac{86}{100}$

**Ans.** (C)



$$\text{Mol of } Br_2 = \frac{21 \times 2}{2} = 21 \text{ mmol}$$

No. of eq. of  $Br_2$  produced in 1<sup>st</sup> Reaction =  $21 \times \frac{5}{3} = 35 \text{ meq.}$



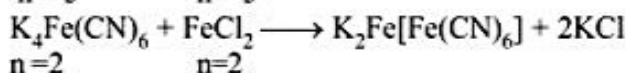
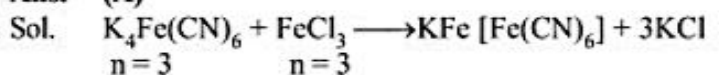
$$\therefore 70 \times M \times \frac{10}{12} = 35$$

$$M = \frac{6}{10} \text{ Ans.}$$

- Q.24** 20 ml of  $K_4Fe(CN)_6$  solution is divided into 2 equal parts. One part is completely reacted with 10 ml of  $FeCl_3$  solution to form  $KFe[Fe(CN)_6]$  &  $KCl$ . Another part of  $K_4Fe(CN)_6$  solution is completely reacted with 20 ml of 0.5 M  $FeCl_2$  solution to produce  $K_2Fe[Fe(CN)_6]$  &  $KCl$ . Molarity of  $FeCl_3$  solution is

- (A) 1M (B) 2M (C)  $\frac{3}{2}$  M (D) 4M

**Ans.** (A)



$$(MV)_{K_4Fe(CN)_6} = (MV)_{FeCl_3}$$

$$10 \times M_1 = M_2 \times 10$$

$$(MV)_{K_4Fe(CN)_6} = (MV)_{FeCl_2}$$

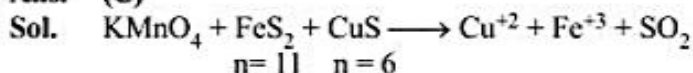
$$10 \times M_1 = 0.5 \times 20$$

$$M_{FeCl_3} = 1 \text{ M Ans.}$$

- Q.25** 20 ml of  $KMnO_4$  solution completely reacts with 10 ml of 1M  $FeS_2$  solution and 20 ml of 1 M  $CuS$  solution to produce  $Cu^{+2}$ ,  $Fe^{+3}$ ,  $SO_2$ . Normality of  $KMnO_4$  solution is

- (A) 57.5 N (B) 6.5 N (C) 11.5 N (D) 8.5 N

**Ans.** (C)



$$\text{Eq. of } KMnO_4 = \text{Eq. of } FeS_2 + \text{Eq. of } CuS$$

$$\frac{N \times V}{1000} = \frac{MV_{FeS_2}}{1000} \times n + \frac{MV_{CuS}}{1000} \times n$$

$$\frac{N \times 20}{1000} = \frac{10 \times 1}{1000} \times 11 + \frac{20 \times 1 \times 6}{1000}$$

$$N = \frac{110 + 120}{20} = \frac{230}{20} = 11.5 \text{ N Ans.}$$

## HYDROGEN & IT'S COMPOUNDS

### HYDROGEN

It is the first element in the periodic table. The position of hydrogen is not definite in the periodic table because it resembles both the alkali metals as well as halogens. At the same time it differs from both in many characteristics.

**Occurrence :** Hydrogen occurs in nature in the free as well as combined state. The earth's crust contains nearly 1% hydrogen by weight. In free state ( $H_2$ ), it occurs only in traces in the atmosphere (1 part in  $10^6$  parts by volume). It is mainly found in the combined state. Important sources are water, acids, alkalies, organic matter, ammonia, hydrogen sulphide, etc.

### Isotopes of Hydrogen

	Protium	Deuterium	Tritium
	Ordinary hydrogen	Heavy hydrogen	Radioactive
Representation	${}^1_1H$	${}^2_1D$	${}^3_1T$
Neutrons	0	1	2
Occurrence	99.98%	0.16%	$10^{-15} \%$

- (i)  $H_2$ ,  $D_2$  and  $T_2$  differ with respect to their properties like (i) rates of diffusion  $H_2$  diffuses 1.414 times faster than  $D_2$  and  $H_2$  diffuses 1.732 times faster than  $T_2$ .

- (ii) **Bond energy and reactivity**

The bond energy of H – H bond is least and hence it is most reactive among the isotopes of hydrogen.

Bond energy  $H_2 < D_2 < T_2$

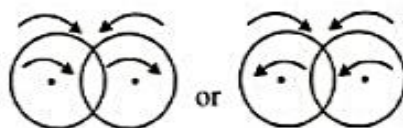
Reactivity  $H_2 > D_2 > T_2$

This difference in the properties of isotopes which arises due to large difference in their atomic masses or molecular masses is called as isotopic effect.

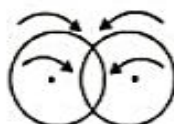
### FORMS OF HYDROGEN

Ordinary hydrogen exists in the form of diatomic molecule which is quite stable and very less reactive.

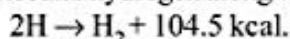
- Active hydrogen :** It is obtained by subjecting molecular hydrogen to silent electric discharge at ordinary temperature and 0.5 mm pressure. This hydrogen, so produced, has great chemical activity. The half-life period of the active hydrogen is similar to that of atomic hydrogen (0.3 sec.)
- Ortho and Para hydrogen :** When the spins of the two protons are in the same direction, the molecule is known as ortho hydrogen, while when the spins of protons are in the opposite directions, hydrogen formed is known as para hydrogen. These two allotropic forms of hydrogen are similar in chemical properties but differ in boiling point, specific heat and thermal conductivities. Ortho hydrogen is more stable than the para hydrogen. Para hydrogen mixed with atomic hydrogen gets converted into the ortho form.

(a) **Ortho hydrogen :**

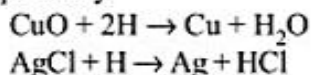
In this molecule of hydrogen both the protons in the two nuclei spin in the same direction.

(b) **Para hydrogen :**3. **Atomic hydrogen :** Molecular hydrogen undergoes thermal dissociation into atomic hydrogen at high temperatures and low pressures.

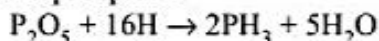
and the heat is stored up in the atoms. Atomic hydrogen, thus produced, when strikes a metallic surface, its atoms recombine to form molecular hydrogen along with the evolution of large amount of heat.

**Properties :**

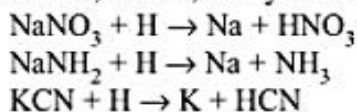
- (i) Atomic hydrogen is highly unstable (half life = 0.3 second).
- (ii) It combines readily with non metals : like S, P, As, Sb, Bi, O<sub>2</sub> and halogens forming corresponding hydride, H<sub>2</sub>O and hydrides respectively.



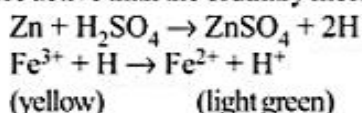
It reduces phosphorus pentoxide to phosphine



It reduces alkali metal salts like nitrates, amides, and cyanides to free metal.

**Uses :**

1. It is used as a strong reducing agent.
2. It is used in the fabrication of atomic hydrogen torch.

2. **Nascent hydrogen :** Hydrogen produced in contact with the substance to be reduced is called nascent (newly born) hydrogen. It is more active than the ordinary molecular hydrogen.

Some of the common sources of nascent hydrogens are

- |   |   |
|---|---|
| (i) A mixture of zinc and dil. H <sub>2</sub> SO <sub>4</sub> | (ii) A mixture of tin and dil. hydrochloric acid. |
| (iii) Aluminium and NaOH.                                     | (iv) Electrolysis of acidified water.             |



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**Illustration**


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1. Hydrogen :  
 (A) resembles in I A since it forms mono valent cation  $H^+$   
 (B) resembles in VII A (halogen family) since it forms monovalent anion  $H^-$   
 (C) resembles in IV A (carbon family) since both have a half filled shell of electron  
 (D) all correct

Ans. D

Sol.  $HCl \rightarrow H$  has +1 oxidation state so it resemble I A group property  
 $NaH \rightarrow H$  has -1 oxidation state so it resemble VII A group property  
 $H (1s^1)$  due to half filled shell of electron it resemble IV A group property

2. Hydrogen gas will not reduce  
 (A) heated cupric oxide (B) heated ferric oxide  
 (C) heated stannic oxide (D) heated aluminium oxide

Ans. D

Sol. Hydrogen gas will not reduce heated aluminium oxide because  $\Delta G$  for this reaction is positive.

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**Exercise**


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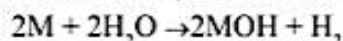
- Q.1 Orthohydrogen and parahydrogen have  
 (A) Same electronic spin, physical and chemical properties  
 (B) Parallel electronic, and nuclear spin with identical physical and chemical properties.  
 (C) Different electronic spin with differences in physical and chemical properties.  
 (D) Opposite electronic spin, different nuclear spin and with different physical properties

Ans. D

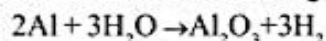
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**METHODS OF PREPARATION OF HYDROGEN ( $H_2$ )**
**1. By action of water with metals.**

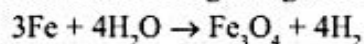
- (a) Active metals like Na, K react at room temperature.



- (b) Less active metals like Ca, Zn, Mg, Al liberate hydrogen only on heating.



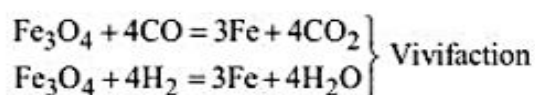
2. **Lane's process:** In this process, steam is passed over hot iron. Iron decomposes steam with the formation of magnetic oxide ( $Fe_3O_4$ ) and hydrogen. The temperature of iron is maintained between 550 to 800°C. This reaction is termed *gassing reaction* and time allotted for this reaction is about 10 minutes.



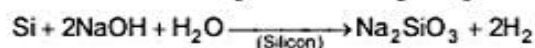
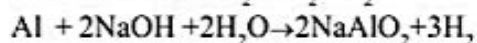
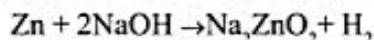
Iron is generated by reducing magnetic oxide with water gas ( $CO + H_2$ ). This reaction is called *vivification* and time allotted for this reaction is about 20 minutes.

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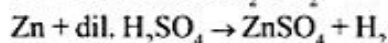
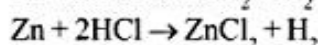
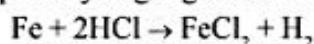




3. **By reaction of metals like Zn, Sn, Al with alkalies.**



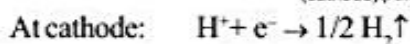
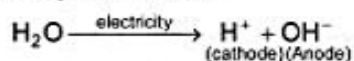
4. **By action of metals with acids.** All active metals which lie above hydrogen in electrochemical series, can displace hydrogen gas from dilute mineral acids.



It must be noted that

- (a) Pure zinc is not used for preparation.
- (b) Conc.  $\text{H}_2\text{SO}_4$  is not used as it oxidizes the liberated  $\text{H}_2$  and produce  $\text{SO}_2$

5. **By electrolysis of water**



6. **Preparation of pure hydrogen.** It can be obtained by

- (a) The action of pure dil.  $\text{H}_2\text{SO}_4$  on pure magnesium ribbon.  

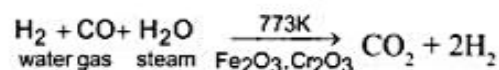
$$\text{Mg} + \text{H}_2\text{SO}_4 \rightarrow \text{MgSO}_4 + \text{H}_2$$
- (b) The electrolysis of a solution of barium hydroxide using nickel electrodes.
- (c) By the action of water on NaH.  

$$\text{NaH} + \text{H}_2\text{O} \rightarrow \text{NaOH} + \text{H}_2$$
- (d) Very pure form of hydrogen is obtained by the action of KOH on scrap aluminum.  

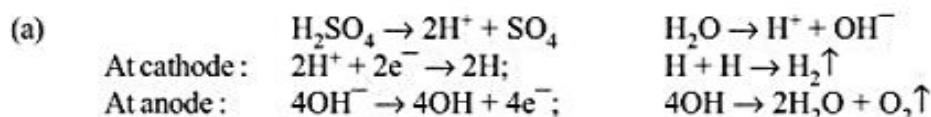
$$2\text{Al} + 2\text{KOH} + 2\text{H}_2\text{O} \rightarrow 2\text{KAlO}_2 + 3\text{H}_2 \uparrow$$

7. **Industrial preparation**

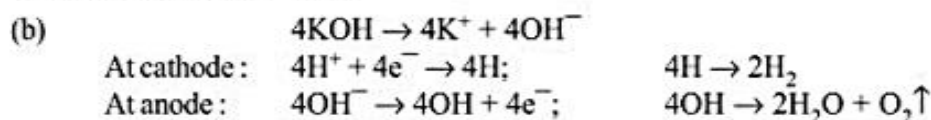
- (a) **Bosch process** - In this method water gas is mixed with steam and passed over heated catalytic mixture of  $\text{Fe}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3$  at 773 K when  $\text{CO}_2$  and  $\text{H}_2$  are obtained. The mixture is compressed to 25 atmospheric pressure and passed into water,  $\text{CO}_2$  dissolves while  $\text{H}_2$  is set free.



- (b) By the electrolysis of water containing a small amount (15 - 20%) of an acid or alkali. Hydrogen is liberated at the cathode (usually iron) while oxygen (a by product) is liberated at anode (usually nickel plated iron rod.) The anode and cathode are separated by an asbestos diaphragm which serves to prevent mixing of hydrogen and oxygen evolved.



It is important to note that sulphate ions are not discharged as their discharge potential is very much higher than that of  $\text{OH}^-$  ions.



Note that  $\text{K}^+$  ions are not discharged at cathode because their discharge potential is high than that of  $\text{H}^+$  ions.

## PROPERTIES

### (a) Physical Properties :

- Hydrogen is colourless, odourless and tasteless gas.
- It is the lightest element and also lightest gas. Its density with respect to air as 1 is 0.0695. One litre of the gas weighs only 0.08987 gm.
- It is sparingly soluble in water.
- Its critical temperature is very low ( $-236.9^\circ\text{C}$ ) at or below which it can be liquefied by the application of a suitable pressure. At  $-258.8^\circ$  it can be liquified.
- Its molecule is diatomic, indicated by the ratio of its specific heats at constant pressure and constant volume ( $C_p/C_v = 1.40$ ).
- It is adsorbed (occluded) by certain metals like Fe, Au, Pt and Pd. Palladium in the powdered state can occlude nearly 1000 times its own volume of hydrogen.

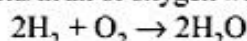
Transportation. Since critical temperature of hydrogen is very low (36.1 K) it can't be liquefied easily. Hence the gas has to be transported under pressure in steel cylinders having almost negligible mass of gas, and can be transported in either of the followed ways.

(i) In the form of hydrolith ( $\text{CaH}_2$ ); 1 pound of  $\text{CaH}_2$  gives  $16.5 \text{ ft}^3$  of  $\text{H}_2$ .

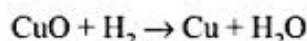
(ii) In the form of anhydrous  $\text{NH}_3$  in light aluminium containers which on cracking gives  $\text{N}_2$  and  $\text{H}_2$  mixture.

### (b) Chemical properties :

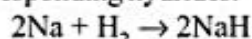
- Reactions of hydrogen are slow at room temperature but rapid at high temperatures. It is neutral towards litmus. It is combustible and burns in air or oxygen with nearly invisible pale blue flame.



- Reducing property. When hydrogen is passed over heated metallic oxides, the latter are reduced to the respective metal.

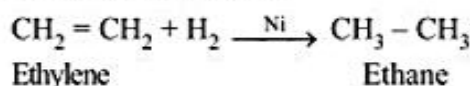


- Reaction with metals and non-metals. It combines with strongly electropositive metals (active metals) like Li, Na and Ca to form corresponding hydrides.



It combines with N, C, O, halogens, S, etc. under suitable conditions to form  $\text{NH}_3$ ,  $\text{CH}_4$ ,  $\text{H}_2\text{O}$ ,  $\text{HX}$  and  $\text{H}_2\text{S}$  respectively.

- Reaction with unsaturated compounds. Hydrogen adds on the double or triple bond in the presence of finely divided Ni to form saturated compounds.



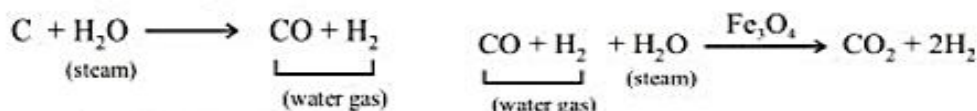
**Illustration**

1. Which of the following pair will not produce dihydrogen gas-  
 (A)  $\text{Cu} + \text{HCl}(\text{dil.})$  (B)  $\text{Fe} + \text{H}_2\text{SO}_4$  (C)  $\text{Mg} + \text{steam}$  (D)  $\text{Na} + \text{alcohol}$

**Ans.** A

**Sol.** The less active metals which lie below hydrogen in electrochemical series can't displace hydrogen gas from dilute mineral acid.

2. The incorrect option regarding the chemical reaction is



- (A) Process is called Lane's process  
 (B) Water gas acts as a reducing agent for  $\text{Fe}_3\text{O}_4$   
 (C)  $\text{Fe}_3\text{O}_4$  shows magnetic property  
 (D)  $\text{Fe}_3\text{O}_4$  can't be concentrated by magnetic separation method

**Ans.** D

**Sol.**  $\text{Fe}_3\text{O}_4$  is a magnetic oxide of iron and it has non-magnetic impurities, so it is concentrated by magnetic separation method.

**Exercise**

1. When dil.  $\text{H}_2\text{SO}_4$  is electrolysed by using platinum electrodes, the gas evolved at the cathode is  
 (A)  $\text{O}_2$  (B)  $\text{SO}_2$  (C)  $\text{SO}_3$  (D)  $\text{H}_2$

**Ans.** D

2. Nascent hydrogen consists of

- (A) hydrogen ions in excited state (B) hydrogen ions with excess energy  
 (C) solvated protons (D) hydrogen atoms with excess energy

**Ans.** D

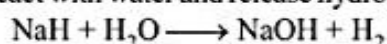
**HYDRIDES**

The compounds of hydrogen with metals or non-metals are called as hydrides. They are classified into different types depending upon their behaviour and nature of bonding.

- (1) **Ionic or Saline hydrides :** Ionic hydrides or salt-like hydrides. The compounds of hydrogen with more electropositive metals like alkali metals and alkaline earth metals are ionic hydrides. They are formed by transfer of electron from metal to hydrogen.

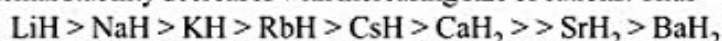
For example :  $\text{LiH}$ ,  $\text{NaH}$ ,  $\text{CaH}_2$ ,  $\text{SrH}_2$  etc.

- (a) They are crystalline solids.  
 (b) They have high melting and boiling points.  
 (c) They conduct electricity in molten state and release hydrogen gas at anode.  
 (d) They react with water and release hydrogen gas and thus act as powerful reducing agents





The thermal stability decreases with increasing size of cations. Thus



- (2) **Covalent or Molecular Hydrides** : The compounds of hydrogen with more electronegative elements or 'p' Block elements are covalent or Molecular hydrides.

For example :  $\text{HCl}$ ,  $\text{H}_2\text{O}$ ,  $\text{CH}_4$ ,  $\text{PH}_3$  etc.

- (a) They are generally soft, with less melting and boiling points.
- (b) They are poor conductors of electricity.
- (c) They release hydrogen on decomposition and thus act as reducing agents.
- (d) Some of them react with water and release hydrogen gas.



- (3) **Interstitial hydrides or Metallic hydrides** : The hydrogen atoms occupy the interstitial spaces of transition elements and hence they are interstitial hydrides. They are nonstoichiometric in nature.

### Illustration

1. Which is not correct statement

- (A) s-block elements, except Be and Mg, form ionic hydride
- (B) Interstitial hydride are nonstoichiometric in nature.
- (C) p-block elements form covalent hydride
- (D) d-, f-block elements form ionic hydride

Ans. D

Sol. Hydrogen atoms occupy the interstitial spaces of d & f block elements & they form interstitial hydrides.

2. Which of the following easily reacts with water producing hydrogen?

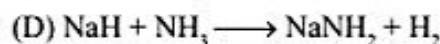
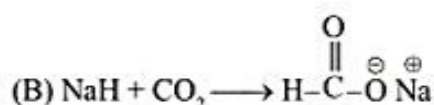
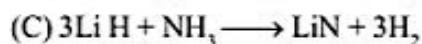
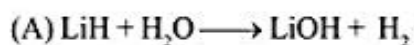
- (A)  $\text{PH}_3$
- (B)  $\text{B}_2\text{H}_6$
- (C)  $\text{CH}_4$
- (D)  $\text{H}_2\text{S}$

Ans. B

Sol.  $\text{B}_2\text{H}_6 + 6\text{H}_2\text{O} \longrightarrow 2\text{B}(\text{OH})_3 + 6\text{H}_2 \uparrow$

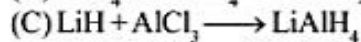
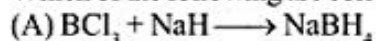
### Exercise

1. Which of the following are correct



Ans. A, B, D

2. Which of the following are correct



(D) All of these

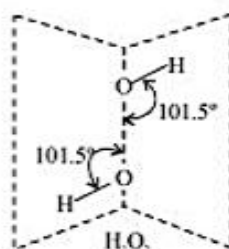
Ans. D



## HYDROGEN PEROXIDE ( $\text{H}_2\text{O}_2$ )

### Structure :

Hydrogen peroxide is best represented as an equilibrium between following two structures. However, all the four atoms do not lie in the same plane, i.e., the  $\text{H}_2\text{O}_2$  molecule is not planar but described as open book structure. The O–O–H bond angle is found to be nearly  $101.5^\circ$ . The O–O single bond distance in  $\text{H}_2\text{O}_2$  is  $1.48 \text{ \AA}$ .

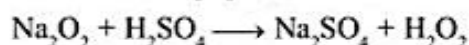


### Tests of $\text{H}_2\text{O}_2$ .

- (i) It liberates iodine from KI solution in the presence of ferrous sulphate.
- (ii) It gives orange red colour with acidified titanium oxide due to formation of pertitanic acid.  
 $\text{Ti}(\text{SO}_4)_2 + \text{H}_2\text{O}_2 + 2\text{H}_2\text{O} \rightarrow \text{H}_2\text{TiO}_4 + 2\text{H}_2\text{SO}_4$
- (iii) When brought in contact with  $\text{H}_2\text{O}_2$  solution, a filter paper with black stain of PbS turns white.
- (iv) It decolourises acidified  $\text{KMnO}_4$  solution.

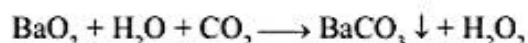
### Preparations of Hydrogen peroxide

- (1) **Merck's Method :**  $\text{Na}_2\text{O}_2$  is gradually added to 20% ice cold  $\text{H}_2\text{SO}_4$

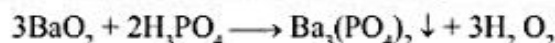


Most of  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  is crystallised out by cooling.

- (2) **By the action of  $\text{CO}_2$  on an ice cold paste of  $\text{BaO}_2$**



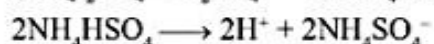
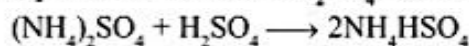
- (3) **By the action of phosphoric acid on  $\text{BaO}_2$**



Impurities (metal ions) present in  $\text{BaO}_2$  are removed as their phosphates.

- Reaction of  $\text{BaO}_2 \cdot 8\text{H}_2\text{SO}_4$  with  $\text{H}_2\text{SO}_4$  (ice cold) also gives  $\text{H}_2\text{O}_2$  but the method is not used as the presence of  $\text{H}_2\text{SO}_4$  & other metal ions (impurities of  $\text{BaO}_2$ ) catalyse the decomposition of  $\text{H}_2\text{O}_2$ .

- (4) **Electrolysis of equimolar mixture of  $\text{H}_2\text{SO}_4$  & ammonium sulphate**



**At cathode:**  $2\text{H}^+ + 2\text{e}^- \longrightarrow \text{H}_2$

**At anode:**  $2\text{NH}_4\text{SO}_4^- \longrightarrow (\text{NH}_4)_2\text{S}_2\text{O}_8 + 2\text{e}^-$   
 (Ammonium persulphate)

Ammonium per sulphate is collected and distilled with water to produce  $\text{H}_2\text{O}_2$



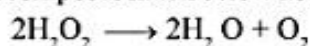
**(5) Auto oxidation of 2-Ethylanthraquinol**

Air is bubbled in 10% solution of 2-Ethylanthraquinol in benzene

2-Ethylanthraquinone obtained is reduced back to 2-Ethylanthraquinol. The solution is concentrated by reduced pressure distillation to get 20%  $\text{H}_2\text{O}_2$ .

**CONCENTRATION OF HYDROGEN PEROXIDE SOLUTION**

Hydrogen prepared by any of the above methods is in the form of dilute aqueous solution. Quite often for a large number of reactions, we need a concentrated solution of  $\text{H}_2\text{O}_2$ . It cannot be concentrated simply by distillation since it decomposes much below its boiling point to give  $\text{H}_2\text{O}$  and  $\text{O}_2$



Further, the process of decomposition is catalysed by the presence by heavy metal ion impurities, dust and rough surfaces. In view of these difficulties, concentration of  $\text{H}_2\text{O}_2$  is carried out carefully in a number of stages.

**Storage of hydrogen peroxide**

The following precautions are taken while storing hydrogen peroxide solution.

- (i) Hydrogen peroxide cannot be stored in glass bottles since the rough surface of glass, alkali metal oxides present in it, and exposure to light catalyse its decomposition. Therefore,  $\text{H}_2\text{O}_2$  is usually stored in coloured paraffin wax coated plastic or teflon bottles.
- (ii) To further ; check the decomposition of  $\text{H}_2\text{O}_2$ , some stabilizer or negative catalyst such as glycerine, acetanilide, phosphoric acid etc. Must also be added.

**Strength of hydrogen peroxide solution**

The strength of aqueous solution of hydrogen peroxide is usually expressed in the following two ways:

- (a) **Percentage strength :** It expresses the amount of  $\text{H}_2\text{O}_2$  by weight present in 100 ml of the solution. For example, a 30% aqueous solution (w/v) of  $\text{H}_2\text{O}_2$  implies that 30 grams of  $\text{H}_2\text{O}_2$  are present in 100 ml of the solution.
- (b) **Volume strength :** The most common method of expression of the strength of an aqueous solution of hydrogen peroxide is in terms of the volume (in ml) of oxygen liberated at N.T.P. by the decomposition of 1 ml of the at sample of hydrogen peroxide.

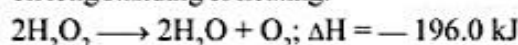
**PROPERTIES OF HYDROGEN PEROXIDE****(a) Physical properties.**

1. Pure hydrogenperoxide is a thick syrupy liquid with pale blue colour.
2. It has a bitter taste.
3. Hydrogen peroxide is more dense ( $1.44\text{g/cm}^3$ ) and more viscous than water. This is due to the reason that the molecules of  $\text{H}_2\text{O}_2$  are even more highly associated through H-bonds than  $\text{H}_2\text{O}$  molecules.
4. Its m.p. is 272.4 K. Since it decomposes vigorously on heating, it is not possible to determine its b.p. at atmosphere pressure. However, its b.p. has been determined to be 423.2 by extrapolation method.
5. It is completely miscible with water, alcohol and ether in all proportions.
6. The dipole moment of  $\text{H}_2\text{O}_2$  is little more (2.1D) than that of  $\text{H}_2\text{O}$  (1.84D).



**(b) Chemical properties.**

1. **Decomposition:** pure hydrogen peroxide is an unstable liquid and decomposes into water and oxygen on long standing or heating.



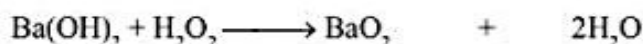
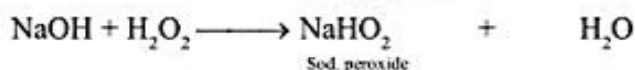
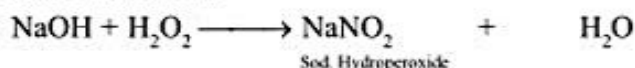
**It is an example of auto-oxidation and auto-reduction.**

The decomposition is further accelerated by the presence of certain metal ions (e.g.  $\text{Fe}^{2+}$ ), metal powders (Co, Au, Ag, Pt etc.), and metal oxides (e.g.  $\text{MnO}_2$ ). Even carbon, rough surfaces and light also catalyse its decomposition.

2. **Acidic Nature:** Pure hydrogen peroxide turns blue litmus red but its dilute solution is neutral to litmus. It thus behaves as a weak acid. Its dissociation constant is  $1.55 \times 10^{-12}$  at 293 K which is only slightly higher than that of water ( $1.0 \times 10^{-12}$ ). Thus, hydrogen peroxide is only a slightly stronger acid than water. Since hydrogen peroxide has two ionizable H-atoms, it forms two series of salts, i.e., hydroperoxides (acidic salts) and peroxides (normal salts).

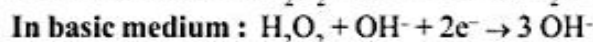
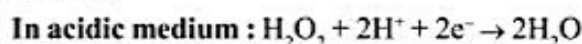


The acidic nature of hydrogen peroxide is shown by its neutralization reaction with hydroxides and carbonates.



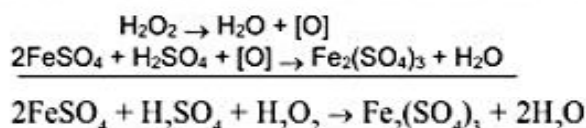
3. **Oxidising and reducing character:** Hydrogen peroxide behaves as an oxidising as well as a reducing agent in both acidic and alkaline solutions. The oxidation state of oxygen in hydrogen peroxide is  $-1$ . It can be oxidised to  $\text{O}_2$  (zero oxidation state) or reduced to  $\text{H}_2\text{O}$  or  $\text{OH}^-$  ( $-2$  oxidation state for oxygen). However, hydrogen peroxide is a powerful oxidising agent but a weak reducing agent.

- (a) **Oxidising character.** Hydrogen peroxide acts as an oxidising agent both in acidic as well as in alkaline medium.

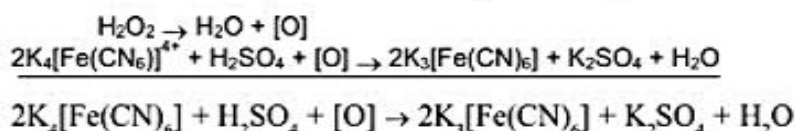


Some important reactions in which hydrogen peroxide acts an oxidising agent are given below;

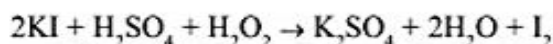
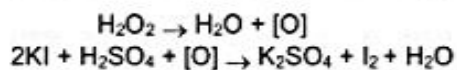
- (i) **It oxidises acidified ferrous sulphate to ferric sulphite**



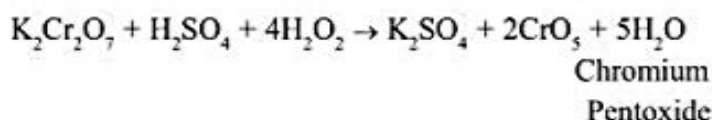
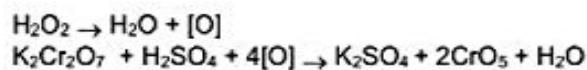
- (ii) **It oxidises acidified potassium ferrocyanide to potassium ferricyanide**



- (iii) It liberates iodine from acidified potassium iodide solution.

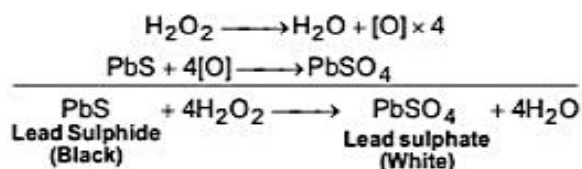


- (iv) Hydrogen peroxide oxidises ice-cold acidified potassium dichromate solution (containing ether) to chromium pentoxide which dissolves in ether producing a blue colouration.



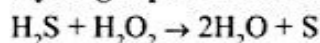
Chromium pentoxide is actually a peroxide having the structure

- (v) Hydrogen peroxide oxidises lead sulphide to lead sulphate

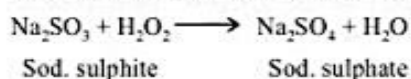


This reaction is used in restoring the white colour of lead paintings which have blackened due to the formation of lead sulphide by the action of  $\text{H}_2\text{S}$  present in the air. On treatment with  $\text{H}_2\text{O}_2$ , lead sulphide (black) changes into lead sulphate (white) and thus the colour of lead paintings is restored.

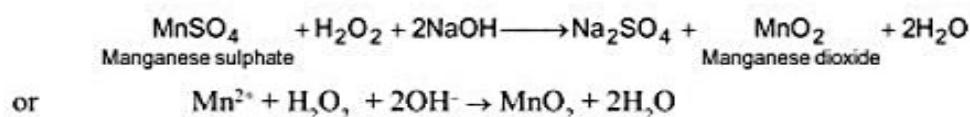
- (vi) Hydrogen peroxide oxidises  $\text{H}_2\text{S}$  to sulphur



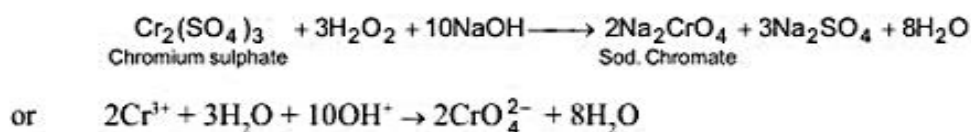
- (vii) It oxidises sulphites, nitrites and arsenites to sulphate, nitrates and arsenates respectively.



- (viii) It oxidises manganese salts to manganese dioxide in alkaline medium.

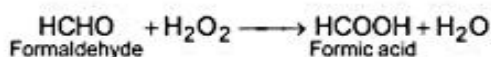


- (ix) It oxidises chromium salts to chromates in alkaline medium.





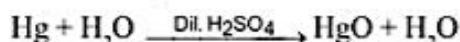
- (x) It oxidises formaldehyde to formic acid



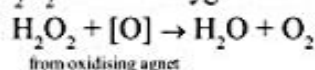
- (xi) It oxidises benzene to phenol



- (xii) It oxidises mercury to mercuric oxide in acidic medium



- (b)
- Reducing character:**
- In presence of strong oxidising agents, hydrogen peroxide behaves as a reducing agent both in acidic as well as alkaline medium. In all these reactions, molecular oxygen is always produced by the combination of
- $\text{H}_2\text{O}_2$
- with the oxygen atom released by the strong oxidising agent:

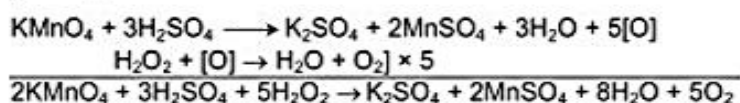


Acidic medium  $\text{H}_2\text{O}_2 \rightarrow 2\text{H}^+ + \text{O}_2 + 2\text{e}^-$

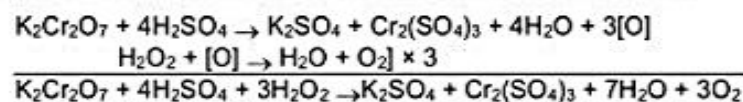
Alkaline medium  $\text{H}_2\text{O}_2 + 2\text{OH}^- \rightarrow 2\text{H}_2\text{O} + \text{O}_2 + 2\text{e}^-$

Some important reactions in which hydrogen peroxide behaves as a reducing agent are given below:

- (i) It reduces acidified potassium permanganate solution. As a result of this reaction, the pink colour of
- $\text{KMnO}_4$
- disappears.

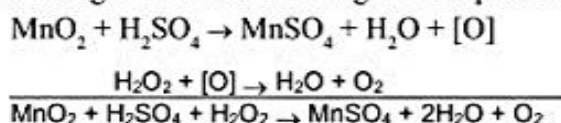


- (ii) It reduces acidified potassium dichromate solution. As a result of this reaction, the orange colour of
- $\text{K}_2\text{Cr}_2\text{O}_7$
- changes to green due to the formation of chromium salt.

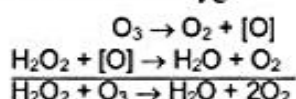


or  $\text{Cr}_2\text{O}_7^{2-} + 8\text{H}^+ + 3\text{H}_2\text{O}_2 \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} + 3\text{O}_2$

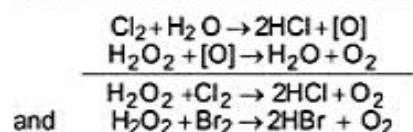
- (iii) It reduces manganese dioxide to manganese sulphate in presence of dil
- $\text{H}_2\text{SO}_4$
- .



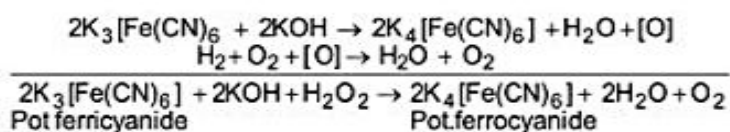
- (iv) It reduces ozone to dioxygen



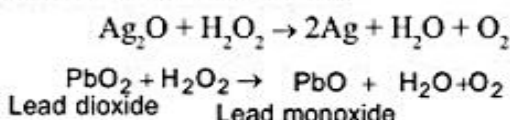
- (v) Chlorine and bromine are reduced to HCl and HBr respectively. This property is called Antichlor.



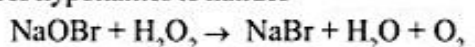
- (vi) It reduces alkaline potassium ferricyanide to potassium ferrocyanide



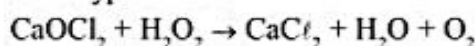
- (vii) It reduces metal oxides to metals, i.e., silver oxide to silver in the alkaline medium. However, lead dioxide is reduced to lead monoxide.



- (viii) It reduces hypohalites to halides



Sod. Hypobromite



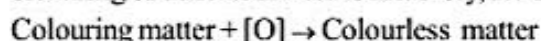
Bleaching powder

#### 4. Bleaching Action.

The bleaching action of hydrogen peroxide is due to the nascent oxygen which it liberates on decomposition.

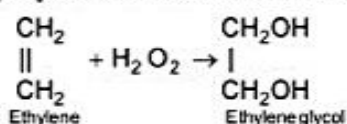


The nascent oxygen combines with colouring matter which, in turn, gets oxidised. It is used for the bleaching of delicate materials like ivory, feather, silk, wool etc.



#### 5. Addition reactions

Hydrogen peroxide reacts with alkenes to form glycols.



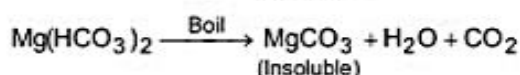
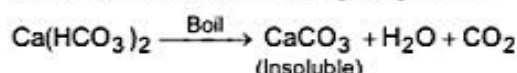
#### Uses of hydrogen peroxide

- It is used for bleaching delicate materials like hair, silk, wool, ivory, textile, wood and paper pulp.
- It is used as an antiseptic under the name perhydrol (30%  $\text{H}_2\text{O}_2$ ) for washing wounds, teeth and ears.
- It is used for restoring the colour of lead paintings which have blackened due to the action of  $\text{H}_2\text{S}$  present in the air on lead paints.
- It is used in the laboratory for detecting the presence of chromium, titanium and vanadium salts with which it yields peroxides of characteristic colours.
- 93%  $\text{H}_2\text{O}_2$  solution is used as an oxidant for rocket fuel and as a propellant for torpedoes and submarines.
- It is used as antichlor (to remove  $\text{Cl}_2$ ) in textile industry to remove excess of chlorine after bleaching operations.
- It is used in the manufacture of many inorganic and organic (sodium perborate, epoxides) compounds.

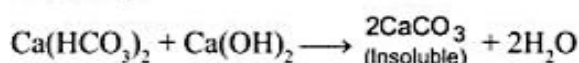




- (a) **Temporary hardness :** This is due to the presence of bicarbonates of calcium and magnesium. Temporary hardness in water is easily removed by boiling, as the bicarbonates decompose readily and the insoluble carbonates are precipitated.



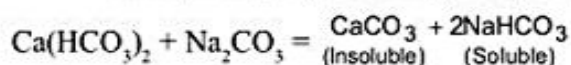
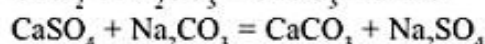
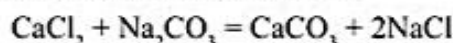
Temporary hardness can also be removed by Clark's process which involves the addition of slaked lime  $[\text{Ca}(\text{OH})_2]$ .



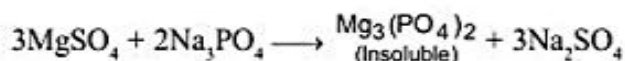
It is essential to add only the calculated amount of  $\text{Ca}(\text{OH})_2$ , because excess will cause artificial hardness.

- (b) **Permanent hardness :** Permanent hardness is introduced when water passes over rocks containing the sulphates or chlorides of both of calcium and magnesium. This type of hardness cannot be removed by boiling or by the addition of slaked lime. Many substances are used for the removal of this type of hardness. The substances used to remove the hardness of water are known as water softeners. The various water softeners are :

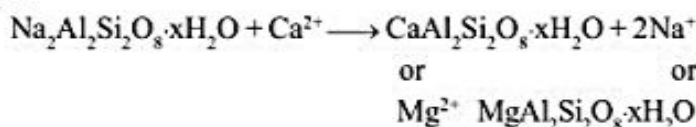
- (i) **Washing soda :** It removes both the temporary and permanent hardness by converting soluble calcium and magnesium compounds into insoluble carbonates.



In place of sodium carbonate, caustic soda or sodium phosphate can also be used.



- (ii) **Permutit :** Permutit is the technical name given to certain hydrated silicates of aluminium and sodium. The sodium ions of permutit are exchanged with calcium and magnesium ions when hard water is passed through it.



These ions can be re-exchanged by treating it with brine (NaCl) solution.



This method is useful for the removal of both temporary and permanent hardness of water.

- (iii) **Calgon** : The complex salt of metaphosphoric acid, sodium hexametaphosphate ( $\text{NaPO}_3$ )<sub>6</sub>, is known as calgon. It is represented as  $\text{Na}_6[\text{Na}_6(\text{PO}_3)_6]$ .



- (iv) **Ion exchange resins :** Ion exchange resins are the most popular water softeners these days. These resins are synthetic substances. The cation exchanger consists of granular insoluble organic acid resin



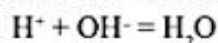
having giant molecules with  $-\text{SO}_3\text{H}$  or  $-\text{COOH}$  groups while the anion exchanger contains giant organic molecules with basic groups derived from amines. Ion exchange resins remove all soluble minerals from water. The hard water is first passed through a bed of cation exchanger, which removes the cations like  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$  and others by exchanging with  $\text{H}^+$  ions.



The water coming from cation exchanger is acidic on account of free  $\text{H}^+$  ions. This water is then passed through another bed containing anion exchanger. This exchanger removes anions like  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  by exchanging with  $\text{OH}^-$  ions.



The  $\text{OH}^-$  ions neutralise the  $\text{H}^+$  ions.



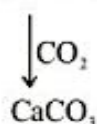
### Illustration

1. Chemical A is used for water softening to remove temporary hardness. A reacts with sodium carbonate to generate caustic soda. When  $\text{CO}_2$  is bubbled through a solution of A, it turns cloudy. What is the chemical formula of A

(A)  $\text{CaCO}_3$  (B)  $\text{CaO}$  (C)  $\text{Ca}(\text{OH})_2$  (D)  $\text{Ca}(\text{HCO}_3)_2$

Ans. C

Sol.  $\text{Ca}(\text{OH})_2 + \text{Na}_2\text{CO}_3 \rightarrow \text{NaOH} + \text{CaCO}_3 \downarrow$



### Exercise

1. Permanent hardness due to  $\text{Mg}^{2+}$  ions is best removed by-  
(A)  $\text{Ca}(\text{OH})_2$  (B)  $\text{Na}_2\text{CO}_3$  (C)  $\text{Na}_2\text{CO}_3 + \text{Ca}(\text{OH})_2$  (D) None of these

Ans. C

2. Permutit is:  
(A) hydrated sodium aluminium silicate  
(B) sodium hexametaphosphate  
(C) sodium silicate  
(D) sodium meta-aluminate

Ans. A

## DEGREE OF HARDNESS

The amount of hardness causing substances (soluble salts of calcium or magnesium) in a certain volume of water measures the extent of hardness or degree of hardness. Hardness of water is always calculated in terms of calcium carbonate although this is never responsible for causing hardness of water because of its insoluble character. The reason for choosing  $\text{CaCO}_3$  as the standard for calculating hardness of water is the ease in calculation as its molecular weight is exactly 100.

Thus the amount of various hardness causing substances in terms of  $\text{CaCO}_3$  can be calculated on the basis of the following relations.

- (i) 1 gm mole or 162 g of  $\text{Ca}(\text{HCO}_3)_2 \equiv$  1 gm mole or 100 g of  $\text{CaCO}_3$
- (ii) 1 gm mole or 111 g of  $\text{CaCl}_2 \equiv$  1 gm mole or 100 g of  $\text{CaCO}_3$
- (iii) 1 gm mole or 136 g of  $\text{CaSO}_4 \equiv$  1 gm mole or 100 g of  $\text{CaCO}_3$
- (iv) 1 gm mole or 146 g of  $\text{Mg}(\text{HCO}_3)_2 \equiv$  1 gm mole or 100 g of  $\text{CaCO}_3$
- (v) 1 gm mole or 95 g of  $\text{MgCl}_2 \equiv$  1 gm mole or 100 g of  $\text{CaCO}_3$
- (vi) 1 gm mole or 120 g of  $\text{MgSO}_4 \equiv$  1 gm mole or 100 g of  $\text{CaCO}_3$

Thus the various types of hardnesses in a water sample may be calculated as below.

Temporary hardness = Hardness due to  $\text{Ca}(\text{HCO}_3)_2$  + Hardness due to  $\text{Mg}(\text{HCO}_3)_2$

Permanent hardness = Hardness due to  $\text{CaCl}_2$  + due to  $\text{CaSO}_4$  + due to  $\text{MgCl}_2$  + due to  $\text{MgSO}_4$

**Degree of hardness** is usually expressed as parts per million (ppm) and thus may be defined as the number of parts by weight of  $\text{CaCO}_3$  (equivalent to calcium and magnesium salts) present in a million (10<sup>6</sup>) parts by weight of water. In short,

1 ppm = 1 part of  $\text{CaCO}_3$  in 10<sup>6</sup> parts of water

From the above definition, we can say that

1 $\text{MgSO}_4$	$\equiv$ 1 $\text{CaCO}_3$	1 $\text{MgCl}_2$	$\equiv$ 1 $\text{CaCO}_3$
120 ppm	100 ppm	95 ppm	100 ppm
1 $\text{CaSO}_4$	$\equiv$ 1 $\text{CaCO}_3$	1 $\text{CaCl}_2$	$\equiv$ 1 $\text{CaCO}_3$
136 ppm	100 ppm	111 ppm	100 ppm

**Ex.1** Determine the degree of hardness of a sample of water containing 30 ppm of  $\text{MgSO}_4$ .

**Sol.** 1  $\text{MgSO}_4 \equiv$  1  $\text{CaCO}_3$   
 120 ppm = 100 ppm  
 $\therefore$  30 ppm = 25 ppm

## HEAVY WATER ( $\text{D}_2\text{O}$ )

Heavy water was first discovered by chemist Urey.

**Methods of preparation :** Following are the methods to prepare heavy water ( $\text{D}_2\text{O}$ ).

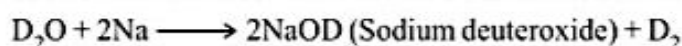
- [1] **By Fractional Distillation of water :** The boiling point of ordinary water is 100°C and the boiling point of  $\text{D}_2\text{O}$  is 101.42°C. Therefore, fractional distillation of water is performed in 40 ft high fractional columns. This process is repeated several times. Lighter part of water is removed on distillation and remaining part is basically heavy water ( $\text{D}_2\text{O}$ ).

- [2] **Fractional Freezing** : In this method heavy water and ordinary water are separated by fractional freezing, because freezing point of water is  $0^{\circ}\text{C}$  and freezing point of heavy water is  $3.82^{\circ}\text{C}$ .
- [3] **Electrolysis of Water** : In this method, 99.5% heavy water is obtained after five steps on repeated electrolysis of NaOH solution in ordinary water.

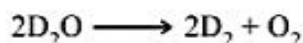
## PROPERTIES

- Physical Properties** : Heavy water is colourless, odourless and tasteless liquid. Its physical constants, like specific gravity, viscosity, melting point, specific heat, are higher than those of ordinary water while surface tension is lower. Solubility of compounds in heavy water is lower as compared to that in ordinary water (approximately 15% lower)
- Chemical Properties** : Chemical reaction of  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  are same O–H bond of  $\text{H}_2\text{O}$  is more polar than O–D bond of  $\text{D}_2\text{O}$ . Therefore the chemical reactions of  $\text{D}_2\text{O}$  are relatively slower as compared to those of  $\text{H}_2\text{O}$ .

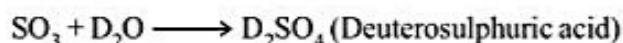
- [a] **With Alkali Metals** : Heavy water liberates  $\text{D}_2$  on reaction with metals, like Na, K, Ca, etc.



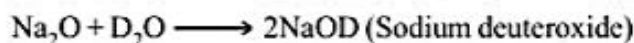
- [b] **Electrolysis** :  $\text{D}_2$  is liberated on electrolysis of heavy water.



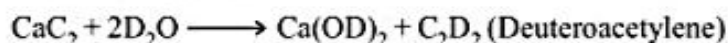
- [c] **With Acid Anhydrides** : Acids are formed on reaction with acid anhydrides, like  $\text{SO}_3$  and  $\text{P}_2\text{O}_5$ .



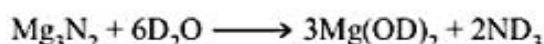
- [d] **With Metal Oxides** : Metal oxides, like  $\text{Na}_2\text{O}$ , form metal deuteroxides on reacting with heavy water.



- [e] **With Carbides** : They form deuterated hydrocarbons. Thus, calcium carbide reacts with heavy water to liberate deuteroacetylene.



- [f] **With Nitrides** : Heavy ammonia is liberated



## Uses of Heavy Water :

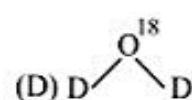
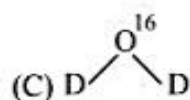
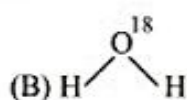
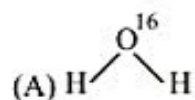
- As moderator in nuclear reactors.
- Electrolysis of heavy water is done for the production of deuterium.
- In the form of a tracer in the studies of mechanism of biochemical reactions in living beings.

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**Illustration**

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1. In which of the following NaCl is more soluble



Ans. A

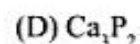
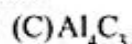
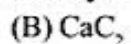
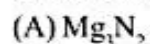
Sol.  $\text{H}-\overset{\text{O}^{16}}{\text{O}}-\text{H}$  due to bond energy of O – H is least.

---

**Exercise**

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1. Deutero methane is obtained by the deuterolysis of



Ans. C

2. Heavy water ( $\text{D}_2\text{O}$ ) is

(A) A product of oxygen and hydrogen

(B) Water of mineral springs

(C) Water obtained by repeated distillation and condensation

(D) Ordinary water containing dissolved salts heavy metals

Ans. C

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## SOLVED EXAMPLES

**Q.1** When a substance A reacts with water, it produces a combustible gas B and a solution of substance C in water. D reacts with this solution C and produces the same gas B on warming. D can also produce gas B on reaction with dilute  $\text{H}_2\text{SO}_4$ . A imparts a deep golden yellow colour to smokeless flame. A, B, C and D respectively are

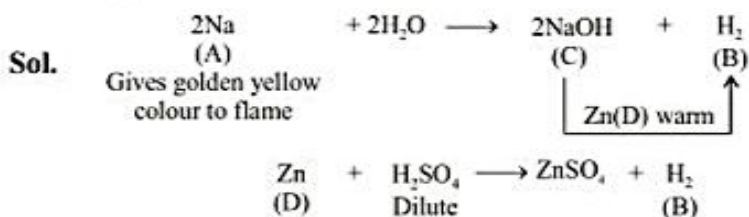
(A) Na,  $\text{H}_2$ , NaOH, Zn

(B) K,  $\text{H}_2$ , KOH, Al

(C) Ca,  $\text{H}_2$ ,  $\text{Ca}(\text{OH})_2$ , Sn

(D)  $\text{CaC}_2$ ,  $\text{C}_2\text{H}_2$ ,  $\text{Ca}(\text{OH})_2$ , Fe

**Ans.** (A)



**Q.2** What is false about  $\text{H}_2\text{O}_2$  ?

(A) Acts both as oxidising and reducing agent

(B) Two OH bonds lie in the same plane

(C) Pale blue liquid

(D) Can be oxidised by  $\text{O}_3$

**Ans.** (B)

**Sol.** Two O-H bonds lie in the different planes.

**Q.3** In which of the following reactions does hydrogen act as an oxidizing agent ?

(A)  $\text{H}_2 + \text{F}_2 \longrightarrow$  (B)  $\text{H}_2 + \text{SiCl}_4 \longrightarrow$  (C)  $\text{Na} + \text{H}_2 \longrightarrow$  (D)  $\text{CuO} + \text{H}_2 \longrightarrow$

**Ans.** (C)

**Sol.** The reaction in which hydrogen accepts the electron or its oxidation number changes from 0 to -1, it acts as an oxidizing agent.  $2\text{Na} + \text{H}_2 \rightarrow 2\text{Na}^+ \text{H}^-$

**Q.4** When  $\text{H}_2\text{O}_2$  is added to ice cold solution of acidified potassium dichromate in ether and the contents are shaken and allowed to stand

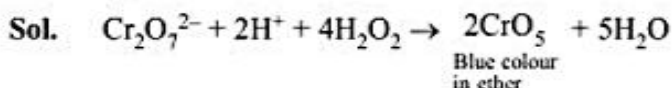
(A) a blue colour is obtained in ether due to formation of  $\text{Cr}_2(\text{SO}_4)_3$

(B) a blue colour is obtained in ether due to formation of  $\text{CrO}_5$

(C) a blue colour is obtained in ether due to formation of  $\text{CrO}_3$

(D) chromyl chloride is formed

**Ans.** (B)



**Q.5** Mass percentage of deuterium in heavy water is

(A) same as that of protium in water

(B) 11.1

(C) 20.1

(D) cannot be predicted

**Ans.** (C)

**Sol.** The formula of heavy water is  $\text{D}_2\text{O}$ , i.e., molecular mass = 20

$$\% \text{ of deuterium} = \frac{4}{20} \times 100 = 20$$

- Q.6** 2 g of aluminium is treated separately with excess of dilute  $\text{H}_2\text{SO}_4$  and excess of  $\text{NaOH}$ . The ratio of volumes of hydrogen evolved under similar conditions of pressure and temperature is  
 (A) 2 : 3 (B) 1 : 1 (C) 2 : 1 (D) 1 : 2

**Ans.** (B)

**Sol.**  $2\text{Al} + 3\text{H}_2\text{SO}_4 \rightarrow \text{Al}_2(\text{SO}_4)_3 + 3\text{H}_2$ ;  
 $2\text{Al} + 2\text{NaOH} + 2\text{H}_2\text{O} \rightarrow 2\text{NaAlO}_2 + 3\text{H}_2$   
 Thus ratio of volumes of hydrogen evolved is 1 : 1

- Q.7** In which reaction, hydrogen peroxide neither acts as an oxidising agent nor a reducing agent ?  
 (A)  $\text{PbS} + \text{H}_2\text{O}_2 \rightarrow$  (B)  $\text{SO}_3 + \text{H}_2\text{O}_2 \rightarrow$  (C)  $\text{PbO}_2 + \text{H}_2\text{O}_2 \rightarrow$  (D)  $\text{Na}_2\text{CO}_3 + \text{H}_2\text{O}_2 \rightarrow$

**Ans.** (D)

**Sol.**  $\text{H}_2\text{O}_2$  behaves as an acid when reacts with  $\text{Na}_2\text{CO}_3$ .  
 $\text{Na}_2\text{CO}_3 + \text{H}_2\text{O}_2 \rightarrow \text{Na}_2\text{O}_2 + \text{CO}_2 + \text{H}_2\text{O}$

- Q.8** Which one of the following reactions does not form gaseous product ?  
 (A)  $\text{PbO}_2 + \text{H}_2\text{O}_2 \rightarrow$  (B)  $\text{PbS} + \text{H}_2\text{O}_2 \rightarrow$  (C)  $\text{Cl}_2 + \text{H}_2\text{O} \rightarrow$  (D)  $\text{Na}_2\text{CO}_3 + \text{H}_2\text{O} \rightarrow$

**Ans.** (B)

**Sol.**  $\text{PbS} + 4\text{H}_2\text{O}_2 \rightarrow \underset{\text{(Solid)}}{\text{PbSO}_4} + \underset{\text{(Liquid)}}{4\text{H}_2\text{O}}$

- Q.9** What is the degree of hardness of a sample of water containing 24 mg of  $\text{MgSO}_4$  (molecular mass 120) per kg of water ?  
 (A) 10 ppm (B) 15 ppm (C) 20 ppm (D) 25 ppm

**Ans.** (C)

**Sol.** 24 mg of  $\text{MgSO}_4$  present in 1000 g of water  
 1000 g water will contain = 24000 mg of  $\text{MgSO}_4 = 24 \text{ g}$  of  $\text{MgSO}_4$   
 $120 \text{ g of } \text{MgSO}_4 \equiv 100 \text{ g of } \text{CaCO}_3$

$$\text{So, } 24 \text{ g of } \text{MgSO}_4 = \frac{100}{120} \times 24 = 20 \text{ g of } \text{CaCO}_3$$

Hardness of water = 20 ppm

- Q.10** In alkaline medium,  $\text{H}_2\text{O}_2$  reacts with  $\text{Fe}^{3+}$  and  $\text{Mn}^{2+}$  separately to give  
 (A)  $\text{Fe}^{4+}$  and  $\text{Mn}^{4+}$  (B)  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  (C)  $\text{Fe}^{2+}$  and  $\text{Mn}^{4+}$  (D)  $\text{Fe}^{4+}$  and  $\text{Mn}^{2+}$

**Ans.** (C)

**Sol.**  $\text{K}_3\text{Fe}(\text{CN})_6$  is reduced by  $\text{H}_2\text{O}_2$  in alkaline medium.  
 $2\text{K}_3\text{Fe}(\text{CN})_6 + 2\text{KOH} + \text{H}_2\text{O}_2 \rightarrow 2\text{K}_4\text{Fe}(\text{CN})_6 + 2\text{H}_2\text{O} + \text{O}_2$   
 $\text{Mn}(\text{OH})_2$  is oxidised by  $\text{H}_2\text{O}_2$  in alkaline medium  
 $\text{Mn}(\text{OH})_2 + \text{H}_2\text{O}_2 \rightarrow \text{MnO}_2 + 2\text{H}_2\text{O}$

# CHEMICAL EQUILIBRIUM

## INTRODUCTION

Whenever we hear the word Equilibrium immediately a picture arises in our mind an object under the influence of two opposing forces. For chemical reactions also this is true. A reaction also can exist in a state of equilibrium balancing forward and backward reactions.

Symbolic representation of any chemical change in terms of reactants and products is called chemical reaction.

**Types of chemical reaction :**

(a) **On the basis of physical state**

Homogeneous reactions	Heterogeneous reaction
All reactants and products are in same phase $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$	Reactants and products are in two or more phase $Zn(s) + CO_2(g) \rightleftharpoons ZnO(s) + CO(g)$

(b) **On the basis of direction**

Reversible reaction	Irreversible reaction
(i) Chemical reaction in which products can be converted back into reactants $H_2 + I_2 \rightleftharpoons 2HI$	Chemical reaction in which products cannot be convert back into reactants $Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$
(ii) Proceed in forward as well as backward direction	Proceed only in forward direction
(iii) These attain equilibrium	These do not attain equilibrium
(iv) Reactant are never completely converted into products	Reactants are nearly completely converted into products
(v) Generally thermal dissociations are held in closed vessel $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$	Generally thermal decompositions are held in open vessel $2KClO_3(s) \rightarrow 2KCl(s) + 3O_2(g)$

(c) **On the basis of speed**

Fast reactions	Slow reactions
(i) Generally these reactions are ionic in nature $HCl + NaOH \rightarrow NaCl + H_2O$ Acid    Base        Salt    Water	Generally these reactions are molecular in nature $H_2 + I_2 \rightarrow 2HI$

(d) **On the basis of heat**

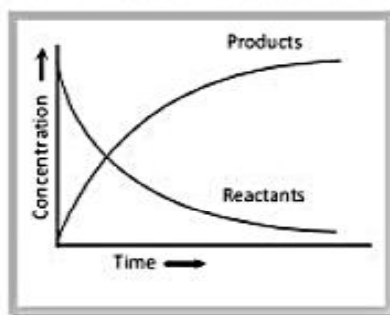
Exothermic reaction	Endothermic reaction
(i) Heat is evolved in these type of chemical reactions $R \rightarrow P + x \text{ kcal}$	Heat is absorbed in these type of chemical reactions $R \rightarrow P - x \text{ kcal}$



It is an experimental fact that most of the process including chemical reactions, when carried out in a closed vessel, do not go to completion. Under these conditions, a process starts by itself or by initiation, continues for some time at diminishing rate and ultimately appears to stop. The reactants may still be present but they do not appear to change into products any more.

## EQUILIBRIUM AND ITS DYNAMIC NATURE

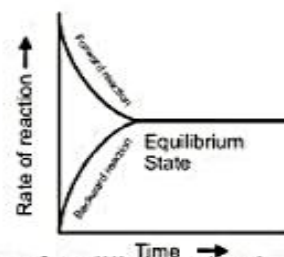
- (1) **Definition :** "Equilibrium is the state at which the concentration of reactants and products do not change with time. i.e. concentrations of reactants and products become constant."
- (2) **Characteristics :** Following are the important characteristics of equilibrium state,



- (i) Equilibrium state can be recognised by the constancy of certain measurable properties such as pressure, density, colour, concentration etc. by changing these conditions of the system, we can control the extent to which a reaction proceeds.
- (ii) Equilibrium state can only be achieved in close vessel, but if the process is carried out in an open vessel equilibrium state cannot be attained because in an open vessel, the reverse process may not take place.
- (iii) Equilibrium state is reversible in nature.
- (iv) Equilibrium state is also dynamic in nature. Dynamic means moving and at a microscopic level, the system is in motion. The dynamic state of equilibrium can be compared to water tank having an inlet and outlet. Water in tank can remain at the same level if the rate of flow of water from inlet (compared to rate of forward reaction) is made equal to the rate of flow of water from outlet (compared to rate of backward reaction). Thus, the water level in the tank remains constant, though both the inlet and outlet of water are working all the time.

- (v) At equilibrium state,

Rate of forward reaction = Rate of backward reaction



- (3) **Types :** Equilibrium in a system implies the existence of the following types of equilibrium simultaneously,
  - (i) Thermal equilibrium : There is no flow of heat from one part to another i.e.  $T = \text{constant}$ .
  - (ii) Mechanical equilibrium : There is no flow of matter from one part to another i.e.  $P = \text{constant}$ .
  - (iii) Physical equilibrium : It is a state of equilibrium between the same chemical species in different phases (solid, liquid and gaseous)
  - (iv) Chemical equilibrium : There is no change in composition of any part of the system with time.

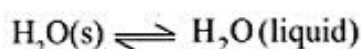


## Physical equilibrium.

The various equilibrium which can exist in any physical system are,

Solid	$\rightleftharpoons$	Liquid
Liquid	$\rightleftharpoons$	Vapour
Solid	$\rightleftharpoons$	Gas(vapour)
Solid	$\rightleftharpoons$	Saturated solution of solid in a liquid
Gas(vapour)	$\rightleftharpoons$	Saturated solution of gas in a liquid

### (1) Solid-liquid equilibrium



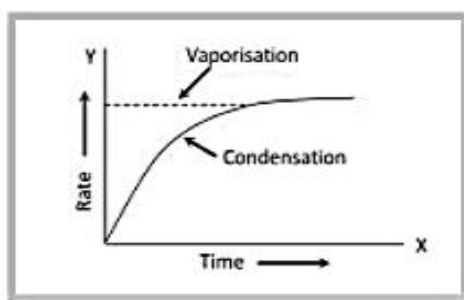
Rate of transfer of molecules from ice to water = Rate of transfer of molecules from water to ice  
 Rate of melting of ice = Rate of freezing of water

### (2) Liquid-vapour equilibrium : When vapour of a liquid exists in equilibrium with the liquid, then Rate of vaporisation = Rate of condensation,



Conditions necessary for a liquid-vapour equilibrium

- The system must be a closed system i.e., the amount of matter in the system must remain constant.
- The system must be at a constant temperature.



- The visible properties of the system should not change with time.

### (3) Solid-vapour equilibrium : Certain solid substances on heating get converted directly into vapour without passing through the liquid phase. This process is called sublimation. The vapour when cooled, gives back the solid, it is called deposition.

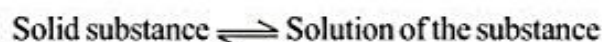


The substances which undergo sublimation are camphor, iodine, ammonium chloride etc.

For example, Ammonium chloride when heated sublimates.



- (4) **Equilibrium between a solid and its solution :** When a saturated solution is in contact with the solid solute, there exists a dynamic equilibrium between the solid and the solution phase.



**Example :** Sugar and sugar solution. In a saturated solution, a dynamic equilibrium is established between dissolved sugar and solid sugar.



At the equilibrium state, the number of sugar molecules going into the solution from the solid sugar is equal to the number of molecules precipitating out from the solution, i.e., at equilibrium,

Rate of dissolution of solid sugar = Rate of precipitation of sugar from the solution.

- (5) **Equilibrium between a gas and its solution in a liquid :** Gases dissolve in liquids. The solubility of a gas in any liquid depends upon the,
- (i) Nature of the gas and liquid.
  - (ii) Temperature of the liquid.
  - (iii) Pressure of the gas over the surface of the solution.

#### Characteristics of chemical equilibrium :

- (a) It is a dynamic equilibrium i.e. at this stage, reaction takes place in both the directions with same speed so, there is no net change.
- (b) At equilibrium the reaction proceeds both the side, equally
- (c) At equilibrium, both reactants and products are present and their concentration do not change with respect to time.
- (d) The state of equilibrium is not effected by the presence of catalyst : It only helps to attain the equilibrium state in less or more time.
- (e) Change in pressure, temperature or concentration favours one of the reactions and thus shifts the equilibrium point in one direction.

#### RATE OF REACTION

In a reaction , there is change in concentration of reactant or product per mole in unit time, it is known as rate of the reaction.

$$\text{Rate of reaction} = \frac{(-) \text{ change in concentration of reactant}}{\text{time}} = - \left( \frac{dc}{dt} \right)_{\text{reactant}}$$

Here negative sign indicate that concentration of reactants decrease with time.

$$\text{Rate of reaction} = + \frac{\text{change in concentration of products}}{\text{time}} = + \left( \frac{dc}{dt} \right)_{\text{product}}$$

Here positive sign indicate that concentration of products increase with time.

**Note :** The concentration change may be positive or negative but the rate of reaction is always positive.

$$\text{Unit of rate of reaction} = \frac{\text{mole/lit.}}{\text{sec}} = \frac{\text{mole}}{\text{lit. sec}} = \text{mole lit}^{-1} \text{sec}^{-1}$$

For example  $A \rightarrow B$

For reactant  $\rightarrow -\frac{d[A]}{dt}$  [concentration decrease with time]

For reactant  $\rightarrow +\frac{d[B]}{dt}$  [concentration increase with time]

[d [A], d [B] are change in concentration of A & B in time dt]

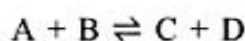
At equilibrium, since there is no net change in concentration of reactant or product.

So rate of reaction is zero.

$$-\frac{d[A]}{dt} = \frac{d[B]}{dt} = 0 \text{ (At equilibrium)}$$

## LAW OF MASS ACTION

- (a) This law was given by **Guldberg and Waage**.
- (b) At a given temperature, the product of the concentration of products each raised to the corresponding stoichiometric coefficients in the balanced chemical equation divided by the product of the concentrations of the reactants raised to the corresponding stoichiometric coefficients has a constant value.



Rate of chemical reaction  $r \propto [A][B]$

$$r = K[A][B]$$

### Mathematical Expression

- (i) **For unitary stoichiometric coefficients**

At the constant temperature, let us consider the following reversible reaction.



According to law of mass action -

Rate of forward reaction

$$r_f \propto [A][B] \quad \text{or} \quad r_f = K_f[A][B]$$

where  $K_f$  is the rate constant of the forward reaction.



Rate of backward reaction

$$r_b \propto [C][D] \quad \text{or} \quad r_b = K_b [C][D]$$

where  $K_b$  is the rate constant of the backward reaction.

At equilibrium:

Rate of reaction = Rate of forward reaction – Rate of backward reaction = 0

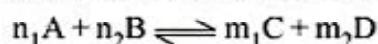
$$K_f [A][B] - K_b [C][D] = 0$$

$$\text{or} \quad \frac{K_f}{K_b} = \frac{[C][D]}{[A][B]}$$

$$\text{or} \quad \boxed{K_{eq} = \frac{[C][D]}{[A][B]}}$$

Here,  $k$  is equilibrium constant of given reversible reaction.

(ii) For non-unitary stoichiometric coefficient



$$r_f = r_b$$

$$K_{eq} = \frac{[C]^{m_1} [D]^{m_2}}{[A]^{n_1} [B]^{n_2}}$$

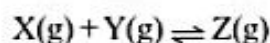
**Note :**  $[A]$ ,  $[B]$ ,  $[C]$ ,  $[D]$  are molar concentration of reactants and products, for dilute solution.

## EQUILIBRIUM CONSTANTS, $K_c$ , $K_p$ , $K_{pc}$ & $K_x$

There are various methods for measuring equilibrium constant in terms of concentration, pressure, mole fraction.

(i) **Equilibrium constant in term of concentration**

Consider an equilibrium reaction as



For this reactions, which is in equilibrium, there exist an equilibrium constant ( $K_{eq}$ ) represented as

$$K_{eq} = \frac{[Z]}{[X][Y]}$$

For the given equilibrium, irrespective of the reacting species (i.e., either  $X + Y$  or  $Z$  or  $X + Z$  or  $Y + Z$

or  $X + Y + Z$ ) and their amount we start with, the ratio,  $\frac{[Z]}{[X][Y]}$  is always constant at a given temperature.

The given expression involves all variable terms (variable term means the concentration of the involved species changes from the start of the reaction to the stage when equilibrium is reaches), so the ratio

$$\frac{[Z]}{[X][Y]} \text{ can also referred as } K_c.$$



$$\therefore K_c = \frac{[Z]}{[X][Y]}$$

Thus, for the given equilibrium, it seems that  $K_{eq}$  and  $K_c$  are same but in actual practice for some other equilibrium, they are not same.

**(ii) Equilibrium constant in terms of pressure**

Assuming that the gases, X, Y and Z behave ideally.

$$PV = nRT$$

$$P = \frac{n}{V} RT = CRT$$

$$C = \frac{P}{RT}$$

$$\therefore [X] = \frac{P_X}{RT}; [Y] = \frac{P_Y}{RT} \text{ and } [Z] = \frac{P_Z}{RT}$$

$$\therefore K_c = \frac{\left(\frac{P_Z}{RT}\right)}{\left(\frac{P_X}{RT}\right)\left(\frac{P_Y}{RT}\right)} = \frac{P_Z \times RT}{P_X \times P_Y}$$

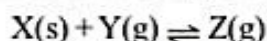
$$\frac{K_c}{RT} = \frac{P_Z}{P_X \times P_Y}$$

The LHS of the above expression is a constant since  $K_c$ ,  $R$  and  $T$ , all are constant. This implies that RHS is also a constant, which is represented by  $K_p$ .

$$\therefore K_p = \frac{P_Z}{P_X \times P_Y}$$

Thus, expression of  $K_p$  involves partial pressures of all the involved species and represents the ratio of partial pressures of product to reactants of an equilibrium reaction.

If the phase of reactant X from gaseous to pure solid. Then the equilibrium reaction can be shown as



Its equilibrium constant ( $K_{eq}$ ) would be

$$K_{eq} = \frac{[Z]}{[X][Y]}$$

The concentration of X is the number of moles of X per unit volume of solid. As we known, the concentration of all pure solids (and pure liquids) is a constant as it is represented by  $d/M$  (where  $d$  and  $M$  represents its density and molar mass). This ratio of  $d/M$  will be a constant whether X is present initially or at equilibrium.

$$K_{eq} [X] = \frac{[Z]}{[Y]}$$

$$\therefore K_c = \frac{[Z]}{[Y]}$$

Thus expression of  $K_c$  involves only those species whose concentration changes during the reaction.

The distinction between  $K_{eq}$  and  $K_c$  is that the expression of  $K_{eq}$  involves all the species (whether they are pure solids, pure liquids, gases, solvents or solutions) while the  $K_c$  expression involves only those species whose concentration is a variable (like gases and solutions). Thus, expression of  $K_c$  is devoid of pure components (like pure solids and pure liquids) and solvents.

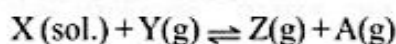
$$K_c = \frac{\frac{P_Z}{RT}}{\frac{P_Y}{RT}} = \frac{P_Z}{P_Y}$$

Since, LHS of the expression is a constant, so the ratio  $\frac{P_Z}{P_Y}$  would also be a constant, represented by  $K_p$ .

$$\therefore K_p = \frac{P_Z}{P_Y}$$

### (iii) Equilibrium constant in terms of both concentration & pressure

Consider the following equilibrium



$$K_c = \frac{[Z][A]}{[X][Y]}$$

If concentration of X, Y, Z and A is expressed in terms of partial pressures

$$\therefore K_c = \frac{\left(\frac{P_Z}{RT}\right)\left(\frac{P_A}{RT}\right)}{[X]\left(\frac{P_Y}{RT}\right)} = \frac{P_Z \times P_A}{[X]P_Y \times RT}$$

$$K_c(RT) = \frac{P_Z \times P_A}{[X]P_Y}$$

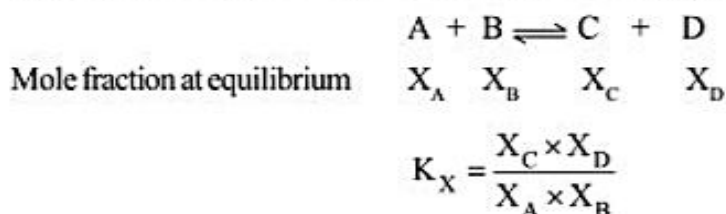
The LHS of the expression is an constant (as  $K_c$ , R and T all constant), which implies that the RHS will also be a constant. But RHS of the expression can neither be called  $K_p$  (as all are not partial pressure terms) nor  $K_c$  (as all are not concentration terms), so such expression that involves partial pressure and concentration terms both are referred as  $K_{pc}$ .

$$\therefore K_{pc} = \frac{P_Z \times P_A}{[X]P_Y}$$

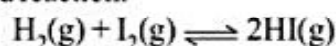
Thus,  $K_p$  can exist only for that equilibrium which satisfies these two conditions.

(a) At least one of the reactant or product should be in gaseous phase and

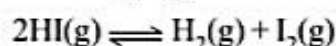
(b) No component of the equilibrium should be in solution phase (Because when solution is present, the equilibrium constant would be called  $K_{pc}$ )

(iv) **Equilibrium constant in terms of moles fraction ( $K_X$ ):****CHARACTERISTICS OF EQUILIBRIUM CONSTANT**

- (i) The expression for equilibrium constant,  $K$  is applicable only when concentrations of the reactants and products have attained their equilibrium values and do not change with time.
- (ii) The value of equilibrium constant is independent of initial concentration of the reactants and product.
- (iii) Equilibrium constant has one unique value for a particular reaction represented by a balanced equation at a given temperature.
- (iv) The equilibrium constant for the reverse reaction is equal to the inverse of the equilibrium constant for the forward reaction.



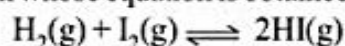
$$K_p = \frac{P_{HI}^2}{P_{H_2} \cdot P_{I_2}}$$



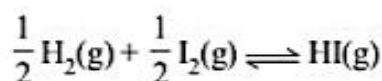
$$K_p' = \frac{P_{H_2} \cdot P_{I_2}}{P_{HI}^2} = \frac{1}{K_p}$$

$$K_p' = \frac{1}{K_p}$$

- (v) The equilibrium constant  $K$ , for a reaction is related to the equilibrium constant of the corresponding reaction whose equation is obtained by multiplying or dividing the equation.

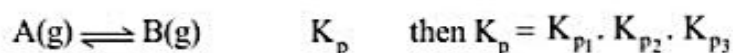
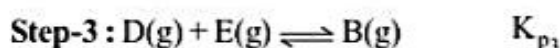
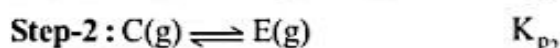
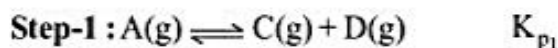
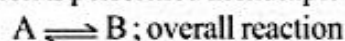


$$K_p = \frac{P_{HI}^2}{P_{H_2} \cdot P_{I_2}}$$



$$K_p^n = \frac{P_{HI}}{P_{H_2}^{1/2} \cdot P_{I_2}^{1/2}} = \sqrt{K_p}$$

- (vi) If reaction is performed in multiple steps



**Factors which do not influence equilibrium constant :**

- (a) Concentration of reactants and products.
- (b) Pressure and volume.
- (c) Presence of catalyst.
- (d) Addition of the inert gas at constant Pressure and volume.

**Factors which influence the equilibrium constant :**

- A. Mode of representation of chemical reaction.
- B. Stoichiometry of reaction.
- C. Temperature.

**A. Mode of representation of reaction –**

If we take reaction  $2\text{HI} \rightleftharpoons \text{H}_2 + \text{I}_2$

Then, we write the value of equilibrium constant  $K_{C_1}$  for the above reaction as following.

$$K_{C_1} = \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2} \quad \dots\dots (i)$$

Now, if we take reaction  $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$

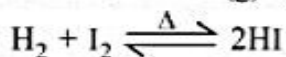
Then, we write the value of equilibrium constant  $K_{C_2}$  for above reaction as following

$$K_{C_2} = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{1}{K_{C_1}} \quad \dots\dots (ii)$$

**B. Stoichiometry of the reaction –**

Method of writing the equation of the reversible reaction is called as stoichiometry of the reaction.

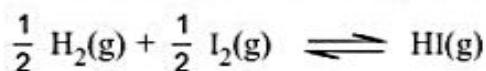
Now, we consider the formation of  $\text{HI(g)}$  by the combination of  $\text{H}_2(\text{g})$  and  $\text{I}_2(\text{g})$ .



The expression of its equilibrium constant is-

$$K_{C_1} = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$$

If the equation of above reaction is written by following method –



The expression for the equilibrium constant is –

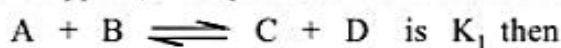
$$K_{C_2} = \frac{[\text{HI}]}{[\text{H}_2]^{1/2}[\text{I}_2]^{1/2}}$$

on the basis of comparing both the equilibrium constant equation.

$$K_{C_2} = \sqrt{K_{C_1}} \quad \text{or} \quad (K_{C_1})^{1/2}$$

**Note :** When we divide a reaction by a factor 'n' in the equation, the value of new equilibrium constant is equal to the root of n of the previous equilibrium constant.

**For Example –** Suppose, the equilibrium constant for the following reaction.





for the reaction



the value of the equilibrium constant  $K_2$  is equal to  $n\sqrt{K_1}$  or  $(K_1)^{1/n}$ .

$$K_2 = K_1^{1/n}$$

### C Temperature –

Increase in temperature favours the endothermic reaction and decrease in temperature favours the exothermic reaction for the forward reaction so for exothermic reactions, the value of  $K_c$  and  $K_p$  decrease with rise in temperature while for endothermic reactions, the value of  $K_c$  and  $K_p$  increases with rise in temperature. This type of variation in equilibrium constant with temperature given by **Van't Hoff** equation as follows -

$$\log K_2 - \log K_1 = \frac{\Delta H}{2.303R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]$$

$$\text{or} \quad \log \frac{K_2}{K_1} = \frac{\Delta H}{2.303R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]$$

Where,

$K_2$  = equilibrium constant at temperature  $T_2$

$K_1$  = equilibrium constant at temperature  $T_1$

$\Delta H$  = Energy of reaction of constant temperature

$R$  = Molar gas constant

According to the temperature, reaction are of three types.

- (a) Non-thermic reaction means  $\Delta H = 0$

$$\log K_2 - \log K_1 = 0$$

$$\log K_2 = \log K_1$$

*There is no effect of temperature on this type of reaction.*

- (b) Endothermic reaction  $\Rightarrow \Delta H = (+)$  ve

$$\log K_2 - \log K_1 = (+) \text{ ve,}$$

$$\text{means } K_2 > K_1$$

*On increasing of temperature, equilibrium constant will also increase for this type of reaction.*

- (c) Exothermic reaction  $\Rightarrow \Delta H = (-)$  ve

$$\log K_2 - \log K_1 = (-) \text{ ve,}$$

$$\text{means } K_2 < K_1$$

*On the increase of temperature equilibrium constant will decreases for exothermic reaction.*

### Units of $K_c$ and $K_p$

The concentration is expressed in the term of moles per litre. Therefore, units of  $K_c$  will be  $(\text{moles litre}^{-1})^{\Delta n}$ .

In the same way, partial pressure are measured by the unit of atmospheres and therefore units of  $K_p$  will be (Atmospheres) $^{\Delta n}$ .

Value of $\Delta n$	Unit of $K_c$	Unit of $K_p$
0	No unit	No unit
> 0	(Moles $l^{-1}$ ) $^{\Delta n}$	(atm) $^{\Delta n_g}$
< 0	(Moles $l^{-1}$ ) $^{\Delta n}$	(atm) $^{\Delta n_g}$

### Relation between $K_p$ and $K_c$

Let us consider the following reaction



The value of  $K_c$  for the reaction is,

$$K_c = \frac{[C]^{m_1} [D]^{m_2}}{[A]^{n_1} [B]^{n_2}}$$

According to gas law  $PV = n RT$

$$P = \left( \frac{n}{v} \right) RT \dots\dots (1)$$

Here  $\frac{n}{v} = \frac{\text{no. of moles}}{\text{lit.}} = [ ] = \text{Active mass}$

$$\therefore K_p = \frac{(p_C)^{m_1} (p_D)^{m_2}}{(p_A)^{n_1} (p_B)^{n_2}}$$

on putting the value of 'p' in the formula of  $K_p$  by the equation (1)

$$K_p = \frac{([C] RT)^{m_1} ([D] RT)^{m_2}}{([A] RT)^{n_1} ([B] RT)^{n_2}}$$

$$K_p = \frac{[C]^{m_1} [D]^{m_2} (RT)^{m_1+m_2}}{[A]^{n_1} [B]^{n_2} (RT)^{n_1+n_2}}$$

$$K_p = K_c (RT)^{(m_1+m_2)-(n_1+n_2)}$$

$$K_p = K_c (RT)^{\Delta n_g}$$

$$[\Delta n = (m_1 + m_2) - (n_1 + n_2)]$$

$\Delta n_g$  = number of moles of gaseous products – number of moles of gaseous reactants.

T = Absolute temperature.

**Illustration**

1. At 700 K, the equilibrium constant  $K_p$ , for the reaction  
 $2\text{SO}_3(\text{g}) \rightleftharpoons 2\text{SO}_2(\text{g}) + \text{O}_2(\text{g})$   
 is  $1.8 \times 10^{-3}$  kPa. What is the numerical value of  $K_C$  for this reaction at the same temperature—  
 (A)  $3.09 \times 10^{-7}$  mole litre $^{-1}$  (B)  $9.03 \times 10^{-7}$  mole litre $^{-1}$   
 (C)  $5.05 \times 10^{-9}$  mole litre $^{-1}$  (D)  $5.05 \times 10^{-5}$  mole litre $^{-1}$

Ans. A

Sol. We know the relationship

$$K_p = K_C(RT)^{\Delta n}$$

Here  $K_p = 1.80 \times 10^{-3}$

$$K_p = \frac{18 \times 10^{-3}}{1013} \text{ atm}$$

$$= 1.78 \times 10^{-5} \text{ atm}$$

$$R = 0.0821 \text{ litre atm K}^{-1} \text{ mol}^{-1}$$

$$\Delta n = 3 - 2 = 1$$

$$T = 700 \text{ K}$$

$$K_C = \frac{K_p}{(RT)^{\Delta n}} = \frac{1.78 \times 10^{-5}}{0.0821 \times 700}$$

$$= 3.09 \times 10^{-7} \text{ mole litre}^{-1}.$$

**Exercise**

1. Equilibrium constant  $K_p$  for the reaction  
 $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$  is 8.21 atm at 727°C,  
 if 10 mole of  $\text{CaCO}_3(\text{s})$  is placed in a 10 L container, what is the weight (in gm) of CaO formed at equilibrium.

Ans. 0056 g

2. The value of  $K_C$  for the reaction  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$  ; is 0.50 at 400° C. What will be the value of  $K_p$  at 400°C when concentration are expressed in mole litre $^{-1}$  and pressure in atmosphere—

- (A)  $1.64 \times 10^{-4}$  (B)  $2.80 \times 10^{-6}$  (C)  $2.80 \times 10^{-4}$  (D)  $1.64 \times 10^{-6}$

Ans A

**APPLICATIONS OF EQUILIBRIUM CONSTANT**

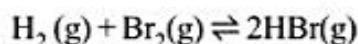
Consider some applications of equilibrium constant and use it to answer question like:

- predicting the extent of a reaction on the basis of its magnitude.
- predicting the direction of the reaction.



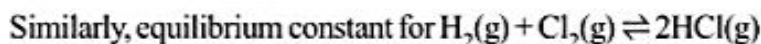
**(i) Predicting the extent of a reaction**

The magnitude of equilibrium constant is very useful especially in reactions of industrial importance. An equilibrium constant tells us whether we can expect a reaction mixture to contain a high or low concentration of product(s) at equilibrium. (It is important to note that an equilibrium constant tells us nothing about the rate at which equilibrium is reached). In the expression of  $K_C$  or  $K_P$ , product of the concentrations of products is written in numerator and the product of the concentrations of reactants is written in denominator. High value of equilibrium constant indicates that product(s) concentration is high and its low value indicates that concentration of the product(s) in equilibrium mixture is low.



$$K_P = \frac{(P_{\text{HBr}})^2}{(P_{\text{H}_2})(P_{\text{Br}_2})} = 5.4 \times 10^{18}$$

The large value of equilibrium constant indicates that concentration of the product, HBr is very high and reaction goes nearly to completion.



is very high and reaction goes virtually to completion.

$$K_C = \frac{[\text{HCl}]^2}{[\text{H}_2][\text{Cl}_2]} = 4.0 \times 10^{31}$$

Thus, large value of  $K_P$  or  $K_C$  (larger than about  $10^3$ ), favour the products strongly. For intermediated values of  $K$  (approximately in the range of  $10^{-3}$  to  $10^3$ ), the concentrations of reactants and products are comparable. Small values of equilibrium constant (smaller than  $10^{-3}$ ), favour the reactants strongly.

At 298 K for reaction,  $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$

$$K_C = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]} = 4.8 \times 10^{-31}$$

The very small value of  $K_C$  implies that reactants  $\text{N}_2$  and  $\text{O}_2$  will be the predominant species in the reaction mixture at equilibrium.

**(ii) Predicting the direction of the reaction.**

The equilibrium constant is also used to find in which direction the reaction will proceed for a given concentration of reactants and products. For this purpose, we calculate the Reaction Quotient ( $Q$ ). The reaction quotient is defined in the same way as the equilibrium constant (with molar concentrations to give  $Q_C$ , or with partial pressure to give  $Q_P$ ) at any stage of reaction. For a general reaction:



$$Q_C = \frac{[\text{C}]^{m_1} [\text{D}]^{m_2}}{[\text{A}]^{n_1} [\text{B}]^{n_2}}$$

Then, if  $Q_C > K_C$ , the reaction will proceed in the backward direction

if  $Q_C < K_C$ , the reaction will move in the forward direction

if  $Q_C = K_C$ , the reaction mixture is already at equilibrium.



In the reaction,  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$ , if the molar concentrations of  $\text{H}_2$ ,  $\text{I}_2$  and  $\text{HI}$  are  $0.1 \text{ mol L}^{-1}$  respectively at  $783 \text{ K}$ , then reaction quotient at this stage of the reaction is

$$Q_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(0.4)^2}{(0.1)(0.2)} = 8$$

$K_c$  for this reaction at  $783 \text{ K}$  is 46 and we find that  $Q_c < K_c$ . The reaction, therefore, will move to right i.e. more  $\text{H}_2(\text{g})$  and  $\text{I}_2(\text{g})$  will react to form more  $\text{HI}(\text{g})$  and their concentration will decrease till  $Q_c = K_c$ .

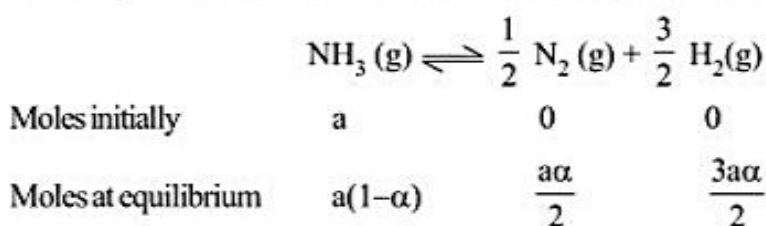
## DEGREE OF DISSOCIATION

Degree of dissociation is the fraction of a mole of the reactant that underwent dissociation. It is represented by ' $\alpha$ '

$$\alpha = \frac{\text{no. of moles of reactant dissociated}}{\text{no. of moles of reactant present initially}}$$

For example,

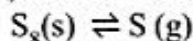
Let the equilibrium reaction is the dissociation equilibrium of  $\text{NH}_3$  into  $\text{N}_2$  and  $\text{H}_2$ .



Here,  $\alpha$  represented the degree of dissociation.

### Illustration

1. 2.56 gm of sulphur  $\text{S}_8(\text{s})$  is taken which is in equilibrium with its vapour according to reaction,



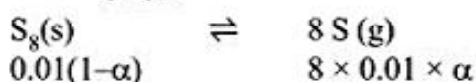
if vapours occupies  $960 \text{ ml}$  at  $1 \text{ atm}$  &  $273 \text{ K}$  then the degree of dissociation of  $\text{S}_8(\text{s})$  will be

[Given :  $R = 0.08$ ]

- (A) 0.5                      (B) 0.55                      (C) 0.4                      (D) 0.44

Ans. B

Sol.  $n_{\text{S}_8} = \frac{2.56}{8 \times 32} = 0.01$



$$PV = nRT$$

$$1 \times \frac{960}{1000} = (0.01 \times 8 \times \alpha) \times 0.08 \times 273$$

$$\alpha = 0.55$$

## Exercise

1. Two moles of ammonia was introduced in an evacuated vessel of 1 litre capacity. At high temperature the gas undergoes partial dissociation according to the equation :



At equilibrium the concentration of ammonia was found to be 1 mole. What is the value of ' $K_C$ '?

Ans.  $1.7 \text{ mol}^2 \text{ l}^{-2}$

### Calculation of $K_p$ & $K_C$

- (a) Homogeneous equilibrium in gaseous phase
- (b) Homogeneous equilibrium in solution phase
- (c) Equilibrium constant for various heterogeneous equilibrium

- (a) Homogeneous equilibrium in gaseous phase

Formation of Nitric Oxide : ( $\Delta n = 0$ )

#### A. Calculation of $K_C$ : -

Suppose the initial concentration of  $\text{N}_2$  and  $\text{O}_2$  is a and b respectively. x is the degree of dissociation.

	$\text{N}_2$	+	$\text{O}_2$	$\rightleftharpoons$	$2\text{NO}$
Initial moles	a		b		0
moles at equilibrium	(a-x)		(b-x)		2x
Active mass ( $\text{mol l}^{-1}$ )	$\frac{(a-x)}{V}$		$\frac{(b-x)}{V}$		$\frac{2x}{V}$

Here, V is the volume of container in litre.

According to the law of mass action

$$K_C = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]}$$

Substituting the values in the above equation

$$K_C = \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{a-x}{V}\right)\left(\frac{b-x}{V}\right)}$$

$$K_C = \frac{4x^2}{(a-x)(b-x)}$$

$K_C$  for this reaction is independent of V of the reaction container.

#### B. Calculation of $K_p$ :

All the things being same as above, except pressure. Let P atmosphere is the pressure at equilibrium.

	$\text{N}_2$	+	$\text{O}_2$	$\rightleftharpoons$	$2 \text{NO}$
Initial moles	a		b		0
moles at equilibrium	(a-x)		(b-x)		2x

Total no. of moles =  $(a-x) + (b-x) + 2x = (a+b)$

The partial pressure of the above three species can be calculated as below-

$$P_{N_2} = \frac{(a-x)P}{(a+b)}$$

$$P_{O_2} = \frac{(b-x)P}{(a+b)}$$

$$P_{NO} = \frac{(2x)P}{(a+b)}$$

According to the law of mass action

$$K_P = \frac{[P_{NO}]^2}{[P_{N_2}][P_{O_2}]}$$

substituting the value of  $P_{NO}$ ,  $P_{N_2}$ ,  $P_{O_2}$  in the above equation of  $K_P$  -

$$K_P = \frac{\left[\frac{(2x)P}{(a+b)}\right]^2}{\left[\frac{(a-x)P}{(a+b)}\right]\left[\frac{(b-x)P}{(a+b)}\right]}$$

$$K_P = \frac{4x^2}{(a-x)(b-x)}$$

### Thermal Dissociation of Phosphorus pentachloride- ( $\Delta n > 0$ )

- A. **Calculation of  $K_C$**  - Suppose one mole of  $PCl_5$  is taken in a closed container of  $V$  litre. Further at equilibrium  $x$  mol of  $PCl_5$  dissociated

	$PCl_5 \rightleftharpoons$	$PCl_3 + Cl_2$
Initial moles	1	0      0
moles at equilibrium	$(1-x)$	$x$ $x$
Concentration ( $\text{mol l}^{-1}$ )	$\frac{1-x}{v}$	$\frac{x}{v}$ $\frac{x}{v}$

According to law of mass action

$$K_C = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

Substituting the values in the above equation.

$$K_C = \frac{\left(\frac{x}{v}\right)\left(\frac{x}{v}\right)}{\left(\frac{1-x}{v}\right)}$$

$$K_C = \frac{x^2}{(1-x)v}$$

The formula of  $K_C$  has  $V$  in the denominator, hence the equilibrium will be affected by  $V$  of the reaction container for the given reaction.

If  $x \ll 1$  then  $1 - x \approx 1$

$$\begin{aligned}\text{So, } K_C &= \frac{x^2}{v} \\ x^2 &= K_C \cdot v \\ x^2 &\propto v \\ \boxed{x &\propto \sqrt{v}}\end{aligned}$$

If we increase the volume, the dissociation  $x$  is also increased.

### B. Calculation of $K_p$ -



Total no. of moles at equilibrium,

$$(1 - x) + x + x = (1 + x) \text{ moles}$$

According to law of mass action

$$K_p = \frac{P_{\text{PCl}_3} \times P_{\text{Cl}_2}}{P_{\text{PCl}_5}}$$

$$\text{At equilibrium } P_{\text{PCl}_3} = \frac{x \times P}{(1+x)}$$

$$P_{\text{Cl}_2} = \frac{x \times P}{(1+x)}$$

$$P_{\text{PCl}_5} = \frac{(1-x)P}{(1+x)}$$

Substituting the values in the above equation of  $K_p$  -

$$K_p = \frac{\left(\frac{x \times P}{1+x}\right) \left(\frac{x \times P}{1+x}\right)}{\frac{(1-x) \times P}{(1+x)}}$$

$$K_p = \frac{x^2 P}{1-x^2}$$

The equation of  $K_p$  is not independent of pressure.

suppose,  $x \ll 1$  then  $1 - x^2 \approx 1$

$$K_p = x^2 P$$

$$x^2 = \frac{K_p}{P}$$

$$x^2 \propto \frac{1}{P}$$

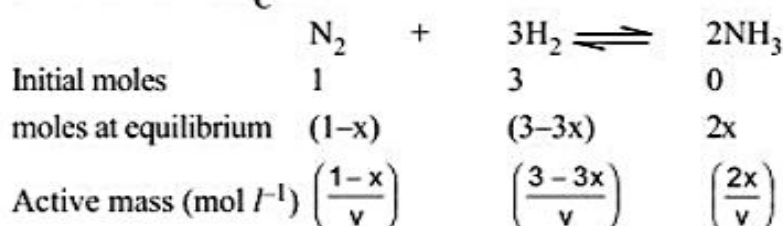


$$x \propto \frac{1}{\sqrt{P}}$$

The degree of dissociation of  $\text{PCl}_5$  is inversely proportional to the square root of pressure so, decrease of pressure increases dissociation of  $\text{PCl}_5$ .

### Formation of Ammonia – ( $\Delta n < 0$ )

#### A. Calculation of $K_C$ : –



According to law of mass action

$$K_C = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$$

Substituting the values in the above equation-

$$K_C = \frac{\left(\frac{2x}{v}\right)^2}{\left(\frac{1-x}{v}\right)\left(\frac{3-3x}{v}\right)^3}$$

$$K_C = \frac{4x^2 v^2}{(1-x)(3-3x)^3}$$

$$K_C = \frac{4x^2 v^2}{27(1-x)^4}$$

The formula of  $K_C$  has  $V$  in the numerator, hence the equilibrium will be affected by  $V$  of the reaction container.

Dependence If,  $x \ll 1$  then,  $(1-x)^4 = 1$

$$K_C = \frac{4x^2 v^2}{27}$$

$$x^2 = \frac{27K_C}{4V^2}$$

$$x^2 \propto \frac{1}{V^2}$$

$$x \propto \frac{1}{V}$$

If we increase the volume of the container the degree of dissociation  $x$  is decreased.

**B. Calculation of  $K_p$  :**

	$N_2$	+	$3H_2$	$\rightleftharpoons$	$2NH_3$
Initial concentration	1		3		0
moles at equilibrium	$(1 - x)$		$(3 - 3x)$		$2x$
Total number of moles at equilibrium	$= (1 - x) + (3 - 3x) + 2x = (4 - 2x)$				

According to the law of mass action

$$K_p = \frac{(P_{NH_3})^2}{(P_{N_2}) \times (P_{H_2})^3}$$

At equilibrium  $P_{NH_3} = \frac{(2x) \cdot P}{(4 - 2x)}$

$$P_{N_2} = \frac{(1 - x) \cdot P}{(4 - 2x)}$$

$$P_{H_2} = \frac{(3 - 3x) \cdot P}{(4 - 2x)}$$

Substituting the values in the above equation of  $K_p$ .

$$K_p = \frac{\left( \frac{2x}{4 - 2x} \cdot P \right)^2}{\left( \frac{1 - x}{4 - 2x} \cdot P \right) \left( \frac{3 - 3x}{4 - 2x} \cdot P \right)^3}$$

$$K_p = \frac{4x^2(4 - 2x)^2}{(1 - x)(3 - 3x)^3 P^2}$$

$$\boxed{K_p = \frac{16x^2(2 - x)^2}{27(1 - x)^4 P^2}}$$

The equation of  $K_p$  is not independent of pressure  
suppose,  $x \ll 1$  then,

$$(1 - x)^4 = 1$$

$$\text{and } (2 - x)^2 = 4$$

$$K_p = \frac{64x^2}{27P^2}$$

$$x^2 \propto P^2$$

$$\boxed{x \propto P}$$

If we increase the pressure the degree of dissociation  $x$  is also increased.

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**Illustration**

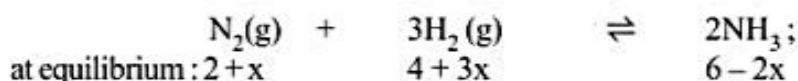

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1. At a certain temperature (T), the equilibrium constant ( $K_C$ ) is 1 for the reaction  

$$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$$
 If 2 moles of  $\text{N}_2$ , 4 moles of  $\text{H}_2$ , 6 moles of  $\text{NH}_3$  & 3 moles of inert gas are introduced into a two litre rigid vessel at constant temperature T. It has been found that equilibrium concentration of  $\text{H}_2$  &  $\text{NH}_3$  are equal then what is the equilibrium concentration of  $\text{N}_2$  (in M)?

Sol. 
$$Q_C = \frac{\left(\frac{6}{2}\right)^2}{\left(\frac{2}{2}\right)\left(\frac{4}{2}\right)^3} \Rightarrow 1.125$$

$\therefore Q_C > K_C$  so reaction will proceed in backward direction.



$\therefore$  At equilibrium  $[\text{H}_2(\text{g})] = [\text{NH}_3(\text{g})]$

$$\frac{4+3x}{2} = \frac{6-2x}{2} \Rightarrow x = 0.4$$

$$\therefore [\text{N}_2(\text{g})] \text{ at equilibrium} = \frac{2+x}{2} \Rightarrow 1.2 \text{ M}$$

---

**Exercise**


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1. At certain temperature pure  $\text{PCl}_5(\text{g})$  is found to be 25% dissociated at total pressure of 50 atm. At what total pressure it is 50% dissociated at same temperature.  
 (A) 10 atm                      (B) 20 atm                      (C) 15 atm                      (D) 30 atm

Ans. A

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**(b) Homogeneous equilibrium in solution phase**


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**Formation of ethyl acetate**

Equilibrium is represented as

$$\text{C}_2\text{H}_5(\text{OH})(l) + \text{CH}_3\text{COOH}(l) \rightleftharpoons \text{CH}_3\text{COOC}_2\text{H}_5(l) + \text{H}_2\text{O}(l)$$

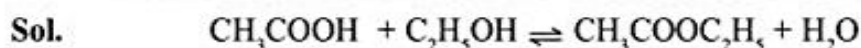
Initial moles	1	1	0	0
Moles at equilibrium	1-x	1-x	x	x
Active mass (mol l <sup>-1</sup> )	$\frac{1-x}{V}$	$\frac{1-x}{V}$	$\frac{x}{V}$	$\frac{x}{V}$

---

$$K_c = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]}{[\text{C}_2\text{H}_5\text{OH}][\text{CH}_3\text{COOH}]} \quad K_c = \frac{\frac{x}{V} \times \frac{x}{V}}{\left(\frac{1-x}{V}\right) \times \left(\frac{1-x}{V}\right)} = \frac{x^2}{(1-x)(1-x)}$$

### Illustration

1. Determine the amount of ester present under equilibrium when 3 moles of ethyl alcohol react with 1 mole of acetic acid, when equilibrium constant of the reaction is 4.



$$\frac{1-x}{V} \quad \frac{3-x}{V} \quad \frac{x}{V} \quad \frac{x}{V}$$

$$K_c = 4 = \frac{\left(\frac{x}{V}\right)\left(\frac{x}{V}\right)}{\left(\frac{1-x}{V}\right)\left(\frac{3-x}{V}\right)}$$

$$3x^2 - 16x + 12 = 0$$

$$x = 0.903$$

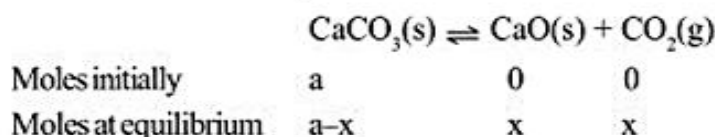
Amount of ester at equilibrium = 0.903 mole

### (c) Equilibrium constant for various heterogeneous equilibrium

Heterogeneous equilibrium results from a reversible reaction involving reactants and product that are in different phases. The law of mass action is applicable to a homogeneous equilibrium and is also applicable to a heterogeneous system.

- (a) Decomposition of solid  $\text{CaCO}_3$  into solid  $\text{CaO}$  and gaseous  $\text{CO}_2$

Let 'a' moles of  $\text{CaCO}_3$  are taken in a vessels of volume 'V' litre at temperature 'T' K.



$$K_{eq} = \frac{[\text{CaO}][\text{CO}_2]}{[\text{CaCO}_3]}$$

As  $\text{CaCO}_3$  and  $\text{CaO}(\text{s})$  are pure solids, so their concentration is unity

$$\therefore K_c = [\text{CO}_2] = \frac{x}{V} \quad \dots\dots\dots(1)$$



Assuming  $\text{CO}_2$  gas to behave ideally at the temperature & pressure of the reaction, the molar concentration of  $\text{CO}_2$  can be written using ideal gas equation as  $\frac{P_{\text{CO}_2}}{RT}$

$$\therefore K_c = \frac{P_{\text{CO}_2}}{RT}$$

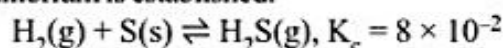
$$K_c(RT) = P_{\text{CO}_2}$$

Since  $K_c$ ,  $R$  and  $T$  are constant, their product will also be a constant referred as  $K_p$ .

$$\therefore K_p = P_{\text{CO}_2} = \frac{xRT}{V} \dots\dots\dots(2)$$

### Illustration

1. At  $87^\circ\text{C}$ , the following equilibrium is established:



If 0.3 mole hydrogen and 2 mole sulphur are heated to  $87^\circ\text{C}$  in a 2 L vessel, what will be the partial pressure of  $\text{H}_2\text{S}$  approximately at equilibrium. [Use  $R = 0.08 \text{ atm.L/mol.K}$ ]

- (A) 0.32 atm      (B) 0.43 atm      (C) 0.62 atm      (D) 4.0 atm

Ans. A

$$\text{Sol. } K_c = \frac{[\text{H}_2\text{S}(\text{g})]}{[\text{H}_2(\text{g})]} \Rightarrow 8 \times 10^{-2} = \frac{x}{0.3 - x}$$

$$0.024 - 0.08x = x$$

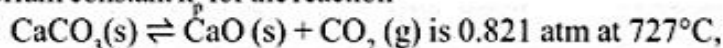
$$0.024 = 1.08x$$

$$x = 0.022$$

$$P_{\text{H}_2\text{S}} = \frac{0.022 \times 0.08 \times 360}{2} \Rightarrow \approx 0.32 \text{ atm}$$

### Exercise

1. Equilibrium constant  $K_p$  for the reaction



if one mole of  $\text{CaCO}_3(\text{s})$  is placed in a 10 L container, what is the weight of  $\text{CaO}$  formed at equilibrium.

- (A) 56 gm      (B) 5.6 gm      (C) 0.56 gm      (D) 0.056 gm

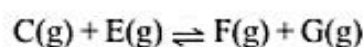
Ans. B

## MULTIPLE EQUILIBRIUM

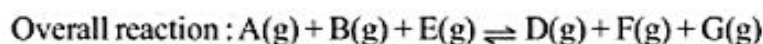
In multiple equilibrium the product molecules (s) in one equilibrium system are involved in a second equilibrium process.



$$K_{C_1} = \frac{[C][D]}{[A][B]}$$



$$K_{C_2} = \frac{[F][G]}{[C][E]}$$



$$K_{C_3} = \frac{[D][F][G]}{[A][B][E]}$$

In this case, one of the product molecule, C(g) of the first equilibrium reaction combines with E(g) to give F(g) and G(g) in another equilibrium reaction, so in the overall, C(g) will not appear on either side.

The equilibrium constant ( $K_{C_3}$ ) of the overall reaction can be obtained if we take the product of the expression of ( $K_{C_1}$ ) and ( $K_{C_2}$ ).

$$K_{C_1} \times K_{C_2} = \frac{[C][D]}{[A][B]} \times \frac{[F][G]}{[C][E]} = \frac{[D][F][G]}{[A][B][E]}$$

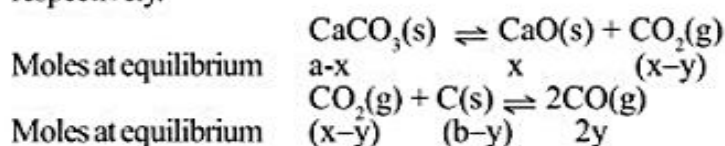
$$\therefore K_{C_1} \times K_{C_2} = K_{C_3}$$

If a equilibrium reaction can be expressed as the sum of two or more equilibrium reactions, the equilibrium constant for the overall reaction is given by the product of the equilibrium constant of the individual reactions.

## SIMULTANEOUS EQUILIBRIUM

In simultaneous equilibrium more than one equilibrium are established in a vessel at the same time and any one of the reactant or product is common in more than one equilibrium, then the equilibrium concentration of the common species in all the equilibrium would be same.

For example, if we take  $\text{CaCO}_3(\text{s})$  and  $\text{C}(\text{s})$  together in a vessel of capacity 'V' litre and heat it at temperature 'T' K, then  $\text{CaCO}_3$  decomposes to  $\text{CaO}(\text{s})$  and  $\text{CO}_2(\text{g})$ . Further, evolved  $\text{CO}_2$  combines with the  $\text{C}(\text{s})$  to give carbon monoxide. Let the moles of  $\text{CaCO}_3$  and carbon taken initially be 'a' and 'b' respectively.



Thus, as  $\text{CO}_2$  is common in both the equilibrium so its concentration is same in both the equilibrium constant expression.

$$\text{Equilibrium constant for first equilibrium, } K_{C_1} = [\text{CO}_2] = \frac{x-y}{V}$$

$$\text{Equilibrium constant for second equilibrium, } K_{C_2} = \frac{[\text{CO}]^2}{[\text{CO}_2]} = \frac{(2y)^2 V}{V^2(x-y)} = \frac{4y^2}{V(x-y)}$$

## EQUILIBRIUM CONSTANT AS PER KINETICS

According to the kinetic theory of gases, in any gaseous system, different gas molecules travel with different speeds. The molecular collision with low energy can never cause bond cleavage and hence can not result the product formation. Only those molecular collision result the formation of product in which the molecules collides with a certain minimum energy.

**Threshold energy** -The minimum amount of energy, which the colliding molecules must possess in order to make the chemical reaction to occur, is known as Threshold energy,  $E_t$ .

**Activation energy** -The minimum amount of energy required to make active participated of almost all molecules in a reaction is called Activation energy,  $E_a$ . The activation energy is equal to  $E_t - E_R$ , where  $E_R$  is the average energy level of reactant molecules.

Activation energy for forward reaction = Threshold energy – Potential energy of reactants

The activation energy of reaction depends on the nature of reactant and temperature. It decreases with increase in temperature but the decrease is so small that it is normally considered temperature independent.

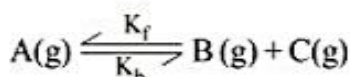
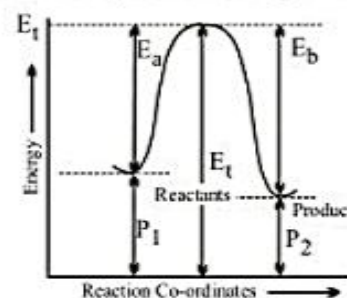
$E_t$  = Threshold energy

$E_a$  = Activation energy of forward reaction

$E_b$  = activation energy of backward reaction

$P_1$  = Potential energy of reactants

$P_2$  = Potential energy of products



$$\frac{-d[A]}{dt} = k_f[A] - k_b[B][C]$$

$$\text{At equilibrium } \frac{-d[A]}{dt} = 0$$

$$\frac{k_f}{k_b} = \frac{[B][C]}{[A]} = K_c$$

According to Arrhenius equation

where  $k = A \cdot e^{-E_a/RT}$  ;  $A$  : pre-exponential factor

$k_f = A_f \cdot e^{-E_{a(f)}/RT}$   $E_a$  : activation energy

$$k_b = A_b \cdot e^{-E_{a(b)}/RT}$$

$$K = \frac{k_f}{k_b} = \frac{A_f e^{-E_{a(f)}/RT}}{A_b e^{-E_{a(b)}/RT}}$$

$$k = A \cdot e^{-\Delta H/RT} \quad \left[ A = \frac{A_f}{A_b} \right]$$



where  $\Delta H = E_{a(f)} - E_{a(b)}$

$$\ln K_1 = \ln A - \frac{\Delta H}{RT_1} \quad (\text{at temp } T_1, K = K_1)$$

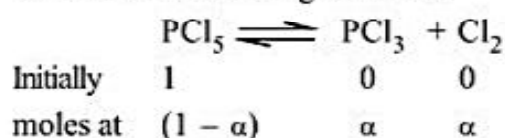
$$\ln K_2 = \ln A - \frac{\Delta H}{RT_2} \quad (\text{at temp } T_2, K = K_2)$$

$$\ln \frac{K_2}{K_1} = \frac{\Delta H}{R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]$$

### CALCULATION OF DEGREE OF DISSOCIATION BY VAPOUR DENSITY MEASUREMENT

Reactions in which there is a change in the number of moles after dissociation, the extent of dissociation can be determined by vapour density measurement.

Consider the following reaction -



equilibrium (' $\alpha$ ' is the degree of dissociation)

Total number of moles at equilibrium =  $(1 - \alpha) + \alpha + \alpha = (1 + \alpha)$

V is the volume occupied by 1 mol of  $\text{PCl}_5(s)$  which have vapour density is 'D' before dissociation and after dissociation is 'd'. Under the same conditions, the volume occupied by  $(1 + \alpha)$  moles at equilibrium would be  $(1 + \alpha) V$  litre.

$$\text{Density} \propto \frac{1}{\text{Volume}}$$

$$D \propto \frac{1}{V} \quad d \propto \frac{1}{(1 + \alpha)V}$$

$$\text{or} \quad \frac{D}{d} = \frac{\frac{1}{V}}{\frac{1}{(1 + \alpha)V}} = (1 + \alpha) \quad \text{or} \quad \alpha = \frac{D}{d} - 1 = \frac{D - d}{d}$$

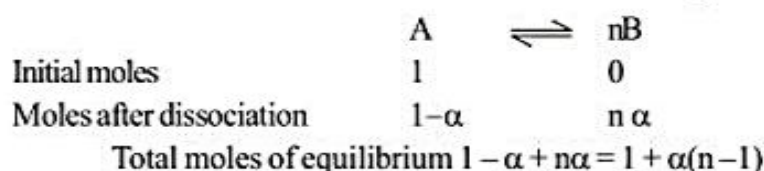
Molecular mass =  $2 \times$  Vapour density

$$\text{so } \alpha = \frac{M_t - M_o}{M_o}$$

where  $M_t$  = calculate molecular mass

$M_o$  = observed molecular mass

**Note :** When one mole of reactant on dissociation gives 'n' moles of gaseous products.





$$\frac{D}{d} = 1(n-1)\alpha, \quad \frac{D-d}{d} = (n-1)\alpha \text{ or } \alpha = \frac{1}{(n-1)} \frac{(D-d)}{d}$$

### Illustration

1.  $\text{N}_2\text{O}_3$  on decomposition gives NO and  $\text{NO}_2$ , they are found to be in equilibrium at 300 K. If the vapour density of such an equilibrium mixture is 23.75, calculate percentage by mass of  $\text{N}_2\text{O}_3$  in the equilibrium mixture?

(A) 80 %                      (B) 60 %                      (C) 40 %                      (D) 20 %

Ans. C

Sol.  $\text{N}_2\text{O}_3 \rightleftharpoons \text{NO} + \text{NO}_2$

$$1 - \alpha \quad \alpha \quad \alpha \quad \therefore \alpha = \frac{D-d}{d(n-1)} = \frac{38-23.75}{23.75(2-1)} = 0.6$$

$$\text{Mass \% of } \text{N}_2\text{O}_3 \text{ in the equilibrium mixture} = \frac{\text{wt. of } \text{N}_2\text{O}_3}{\text{Total wt.}} \times 100$$

$$= \frac{0.4 \times 76}{0.6 \times 30 + 0.6 \times 46 + 0.4 \times 76} \times 100 = 40 \%$$

### Exercise

1. If  $\text{PCl}_5$  is 80% dissociated at  $250^\circ\text{C}$  then its vapour density at room temperature will be

(A) 56.5                      (B) 104.25                      (C) 101.2                      (D) 52.7

Ans. B

## GIBB'S FREE ENERGY AND EQUILIBRIUM CONSTANT

Gibb's free energy (G) of a system is defined as the thermodynamic quantity of the system, the decrease in whose value during a process is equal to useful work done by the system.

Standard free energy change is defined as the free energy change for a process at 298 K and 1 atm pressure in which the reactants in their standard state are converted to products in their standard state. It is denoted as  $\Delta G^\circ$ .

**Note :** Standard free energy change ( $\Delta G^\circ$ ) is not the free energy change at equilibrium.  $\Delta G^\circ$  is related to K (equilibrium constant) by the relation

$$\Delta G^\circ = -RT \ln K.$$

$$\Delta G^\circ = -2.303 RT \log K.$$

K may either be  $K_c$  or  $K_p$ .

The units of  $\Delta G^\circ$  depends only on RT. T is always in Kelvin, and if R is in Joules,  $\Delta G^\circ$  will be in joules and if R is calories then  $\Delta G^\circ$  will be in calories.

### Illustration

1. NO and  $\text{Br}_2$  at initial partial pressures of 98.4 and 41.3 torr, respectively, were allowed to react at 300K. At equilibrium the total pressure was 110.5 torr. Calculate the value of the equilibrium constant and the standard free energy change at 300 K for the reaction  $2\text{NO}(\text{g}) + \text{Br}_2(\text{g}) \rightleftharpoons 2\text{NOBr}(\text{g})$ .

<b>Sol.</b>	$2\text{NO}(\text{g})$	+	$\text{Br}_2(\text{g})$	$\rightleftharpoons$	$2\text{NOBr}(\text{g})$
Initial pressure	98.4		41.3		0
At equilibrium	$98.4 - x$		$41.3 - \frac{x}{2}$		x

Total pressure at equilibrium is 110.5 torr

$$\therefore 98.4 - x + 41.3 - \frac{x}{2} + x = 110.5$$

$$x = 58.4 \text{ torr}$$

$$\text{Now, } 1 \text{ atm} = 760 \text{ torr; } \therefore x = 7.68 \times 10^{-2} \text{ atm}$$

$$P_{\text{NOBr}} = 7.68 \times 10^{-2} \text{ atm; } p_{\text{NO}} = 98.4 - x = 40 \text{ torr} = 5.26 \times 10^{-2} \text{ atm}$$

$$P_{\text{Br}_2} = 41.3 - \frac{x}{2} = 12.1 \text{ torr} = 1.59 \times 10^{-2} \text{ atm}$$

$$K_p = \frac{[p_{\text{NOBr}}]^2}{[p_{\text{NO}}]^2 [p_{\text{Br}_2}]} = \frac{(7.68 \times 10^{-2})^2}{(5.26 \times 10^{-2})^2 (1.59 \times 10^{-2})} = 134 \text{ atm}^{-1}$$

$$\Delta G^\circ = -2.303 RT \log K = -2.303 (1.99) \times 10^{-3} (300) (\log 134)$$

$$= -2.92 \text{ k cal} = 12.2 \text{ k J.}$$

[If R is used as 1.99 cal/mol K, then  $\Delta G^\circ$  will be in cal. If R is used as 8.314 J/mol K, then  $\Delta G^\circ$  will be in joules. But  $K_p$  must be in  $(\text{atm})^{\Delta n}$ ]

### Exercise

1. For the reaction takes place at certain temperature  $\text{NH}_4\text{HS}(\text{s}) \rightleftharpoons \text{NH}_3(\text{g}) + \text{H}_2\text{S}(\text{g})$ , if equilibrium pressure is X bar, then  $\Delta_r G^\circ$  would be  
(A)  $-2 RT \ln X$  (B)  $-RT \ln (X - \ln 2)$  (C)  $-2 RT (\ln X - \ln 2)$  (D) None of these

Ans. C

## LE CHATELIER PRINCIPLE

Chemical equilibrium represents a balance between forward and reverse reactions. In most cases, this balance is quite delicate. Changes in concentration, pressure, volume and temperature may disturb the balance and shift the equilibrium position so that more or less of the desired product is formed. There is a general rule (named Le Chatelier principle) that helps us to predict the direction in which an equilibrium reaction will move when a change in concentration, pressure, volume or temperature occurs. Le Chatelier's principle states that if an external stress is applied to a system at equilibrium, the system adjusts in such a way that the stress is partially offset.

The word "stress" here implies a change in concentration, pressure, volume, addition of an inert gas or temperature that removes a system from the equilibrium state.

Le Chatelier principle can be explained using the following equilibrium reaction



Let the moles of  $\text{PCl}_5$ ,  $\text{PCl}_3$  and  $\text{Cl}_2$  at equilibrium be  $a$ ,  $b$  and  $c$  respectively. Also let the volume of the container in which equilibrium is established be ' $V$ ' litre and the total pressure of the system at equilibrium be  $P_T$  atm.

$$K_p = \frac{(P_{\text{PCl}_3})(P_{\text{Cl}_2})}{(P_{\text{PCl}_5})} = \frac{\left(\frac{b}{a+b+c} \times P_T\right) \left(\frac{c}{a+b+c} \times P_T\right)}{\left(\frac{a}{a+b+c} \times P_T\right)}$$

$$\therefore K_p = \frac{bc \times P_T}{a(a+b+c)} \quad \dots\dots\dots(1)$$

The total pressure of the system ( $P_T$ ) can be given as (assuming all gases at equilibrium behave ideally under the given conditions)

$$P_T = \frac{(a+b+c) RT}{V}$$

$$\therefore \frac{P_T}{(a+b+c)} = \frac{RT}{V}$$

Inserting the value of  $\frac{P_T}{(a+b+c)}$  in equation (i), we get

$$K_p = \frac{bc \times RT}{a \times V} \quad \dots\dots\dots(2)$$

*Let us examine the effect of change of certain parameters like moles of reactant, moles of product, volume, temperature, addition of inert gas and addition of catalyst on the given equilibrium.*



**(a) Change in number of moles of reactant**

If we add 'd' moles of  $\text{PCl}_3$  to the equilibrium mixture, the equilibrium would be disturbed and the expression  $\frac{bc \times RT}{(a+d)V}$  becomes  $Q_p$ . As  $Q_p < K_p$ , so the net reaction moves in the forward direction till  $Q_p$  becomes equal to  $K_p$ .

*Thus for any equilibrium, when more reactant is added to (or some product is removed from) an equilibrium mixture, the net reaction moves in the forward direction (as  $Q < K$ ) to establish a new equilibrium state.*

**(b) Change in number of moles of product**

Let 'd' moles of  $\text{PCl}_3$  (or  $\text{Cl}_2$ ) are added to the equilibrium. The equilibrium would be under stress and thus the expression  $\frac{(b+d)c \times RT}{a \times V}$  would become  $Q_p$ . Since  $Q_p > K_p$ , so the net reaction moves in the reverse direction till  $Q_p$  becomes same as  $K_p$ .

*Thus for any equilibrium, when product is added to (or some reactant is removed from) an equilibrium mixture, the net reaction moves in the reverse (backward) direction (as  $Q > K$ ) to establish a new equilibrium state.*

**(c) Change in volume**

Let the volume of the container be increased from V to V' litre. The equilibrium would be disturbed and the expression  $\frac{bc \times RT}{a \times V'}$  becomes  $Q_p$ . The value of  $Q_p$  is less than  $K_p$ , so the net reaction moves in the forward direction to establish new equilibrium. But when the volume of the container is decreased, the reaction moves in the backward direction to again attain the equilibrium state.

*Thus for any equilibrium, on increasing the volume of the container, the net reaction shifts in the direction of more moles of the gases while on decreasing the volume of the vessel, the reaction goes in the direction of fewer moles of the gases.*

**(d) Addition of an inert gas**

The effect of addition of an inert gas can be studied under two conditions (i), at constant volume (ii) at constant pressure.

**(i) At constant volume**

Let 'd' moles of an inert gas are added to the equilibrium mixture at constant volume. The total number of moles of the system increases so is the pressure of the system but the partial pressure of all the species

would still be same. Let the total pressure becomes  $P_T'$  then  $\frac{P_T'}{(a+b+c+d)} = \frac{RT}{V}$ . As R, T and V are

constant, so the expression  $\frac{bc \times RT}{a \times V}$  would still be equal to  $K_p$ . As,  $Q_p = K_p$ , then net reaction does not move at all.

*Thus for any equilibrium when an inert gas is added at constant volume, the equilibrium remains unaffected whether the equilibrium reactions have  $\Delta n$  equal to zero or non-zero.*



**(ii) At constant pressure**

Now, let 'd' moles of an inert gas are added to the equilibrium mixture at constant pressure to keep the pressure constant, volume of the vessel should increase. Let the volume of the vessel increase from V

to V' litre. So, the expression  $\frac{bc \times RT}{a \times V}$  becomes  $Q_p$ . As the value of  $Q_p < K_p$ , so the net reaction moves in the forward direction to establish new equilibrium state. Thus, *addition of an inert gas at constant pressure has the same effect as produced by the increased volume of the container.*

Thus, for equilibrium having  $\Delta n = 0$ , when an inert gas is added at constant pressure, the equilibrium remains unaffected (since V does not appear in the expression of  $K_p$ ) while for equilibrium having  $\Delta n \neq 0$ , the addition of an inert gas at constant pressure causes reaction to move in the direction of more moles of the gases.

**(e) Addition of a catalyst**

A catalyst enhances the rate of a reaction by lowering the reactions' activation energy. Actually a catalyst lowers the activation energy of the forward reaction and the reverse reaction to the same extent, *so the presence of a catalyst does not alter the equilibrium constant nor does it shift the position of an equilibrium system.* Adding a catalyst to a reaction mixture that is not at equilibrium will simply cause the mixture to reach equilibrium faster.

**(f) Change in temperature**

If  $K_p$  increases, the net reaction moves forward while if  $K_p$  decreases, the net reaction moves backward.

The variation of  $K_p$  with temperature is given by Van't Hoff equation as

$$\log \frac{K_{T_2}}{K_{T_1}} = \frac{\Delta H}{2.303R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right] \text{ where } T_2 > T_1$$

All reactions are either endothermic or exothermic in nature. For an endothermic reactions,  $\Delta H$  is positive and with an increase in temperature of the system to  $T_2$  K from  $T_1$  K, the RHS of the expression becomes positive. Thus, equilibrium constant at higher temperature ( $K_{T_2}$ ) would be more than the equilibrium constant at lower temperature ( $K_{T_1}$ )

But for an exothermic reaction,  $\Delta H$  is negative and on increasing the temperature of the system from  $T_1$  K to  $T_2$  K, the RHS of the expression becomes negative. So the equilibrium constant at higher temperature would be less than equilibrium constant at lower temperature.

The given equilibrium,  $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$  is endothermic in nature. So, with the increase of temperature from  $T_1$  K to  $T_2$  K,  $K_p$  and  $Q_p$  both increase. Therefore, equilibrium shifts in the forward direction.

Thus, for an endothermic reaction ( $\Delta H = \text{positive}$ ), with the increase of temperature, net reaction moves in the forward direction and the decrease in temperature favours backward reaction while for an exothermic reaction ( $\Delta H = \text{negative}$ ), net reaction moves in the backward direction with the increase of temperature and in forward direction with the decrease temperature.

In general, with the increases of temperature, net reaction moves in that direction where the heat is absorbed and the effect of increasing temperature is nullified.

**(g) Change in more than one parameter**

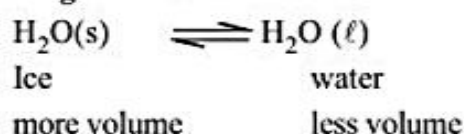
For the given equilibrium, if the number of moles of  $\text{PCl}_3$  is increased four folds and the volume of the vessel is doubled, then the equilibrium would be disturbed. The expression  $\frac{4b \times c \times RT}{a \times 2V}$  would become

$Q_p$ . Since  $Q_p > K_p$ , so the net reaction moves in reverse direction till  $Q_p$  becomes equal to  $K_p$ .

Thus, when two or more parameters are simultaneously changed for any equilibrium, find the changed value of  $Q$  and  $K$  and compare them. If  $Q = K$ , there will be no effect on the reaction, if  $Q > K$ , the net reaction moves in the backward direction. While if  $Q < K$ , net reaction moves in the forward direction.

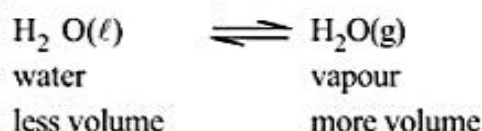
**Application of Le chatelier principle on physical equilibrium**

**A. Melting of Ice :**



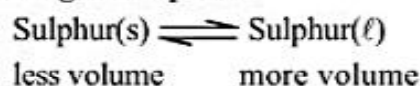
If we increase the pressure, the equilibrium will in the direction of less volume. Hence, the rise of pressure, more ice will melt into water i.e. melting point of ice is decreased by rise of pressure.

**B. Vaporization of liquid -**



Vaporization of a liquid is endothermic process in the nature i.e. the evaporation of a liquid into its vapour is completed by absorption of heat, so the rise of temperature will favour vaporization. On the other hand in this process, on increase of pressure the equilibrium will shift in the direction of less volume means water cannot be converted into vapour and boiling point increases.

**C. Melting of Sulphur :**



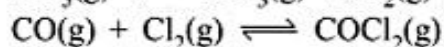
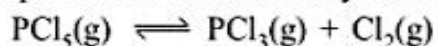
On increase in pressure, the equilibrium will shift towards less volume means solid is not converted into liquid and thus, melting point of sulphur increases.

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**Illustration**


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1. Following two equilibrium is simultaneously established in a container



If some Ni(s) is introduced in the container forming Ni (CO)<sub>4</sub> (g) then at new equilibrium

- (A) PCl<sub>3</sub> concentration will increase  
 (B) PCl<sub>3</sub> concentration will decrease  
 (C) Cl<sub>2</sub> concentration will remain same  
 (D) CO concentration will remain same

Ans. B

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**Exercise**


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1. For the gas phase exothermic reaction,  $\text{A}_2 + \text{B}_2 \rightleftharpoons \text{C}_2$ , carried out in a closed vessel, the equilibrium moles of A<sub>2</sub> can be increased by

- (A) increasing the temperature                      (B) decreasing the pressure  
 (C) adding inert gas at constant pressure        (D) removing some C<sub>2</sub>

Ans. A, B, C

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### $K_p$ & $K_c$ for different reactions

S. No	Reaction	$\Delta n$	Relation between $K_p$ and $K_c$	Values of $K_c$	Values of $K_p$	Unit of $K_c$	Unit of $K_p$	$\Delta H$	Condition for obtaining more product
1.	$H_2 + I_2 \rightleftharpoons 2HI$	0	$K_p = K_c(RT)^0$	$\frac{4x^2}{(a-x)(b-x)}$	$\frac{4x^2}{(a-x)(b-x)}$	None	None	-ve (exothermic)	Low temperature No pressure High concentration of reactant
2.	$2HI \rightleftharpoons H_2 + I_2$	0	$K_p = K_c(RT)^0$	$\frac{x^2}{4(1-x)^2}$	$\frac{x^2}{4(1-x)^2}$	None	None	+ve (endothermic)	High temperature No pressure High concentration of reactant
3.	$PCl_5 \rightleftharpoons PCl_3 + Cl_2$	+1	$K_p = K_c(RT)^1$	$\frac{x^2}{(1-x)v}$	$\frac{x^2 p}{1-x^2}$	$\text{mol L}^{-1}$	atm	+ve (endothermic)	High temperature Low pressure High concentration of reactant
4.	$N_2O_4 \rightleftharpoons 2NO_2$	+1	$K_p = K_c(RT)^1$	$\frac{4x^2}{(1-x)v}$	$\frac{4x^2 p}{1-x^2}$	$\text{mol L}^{-1}$	atm	+ve (endothermic)	High temperature Low pressure High concentration of reactant
5.	$2NH_3 \rightleftharpoons N_2 + 3H_2$	+2	$K_p = K_c(RT)^2$	$\frac{27x^4}{4(1-x)^2 v^2}$	$\frac{27x^4 p^2}{16(1-x)^2 (1-x)^2}$	$\text{mol}^2 \text{L}^{-2}$	atm <sup>2</sup>	+ve (endothermic)	High temperature Low pressure High concentration of reactant
6.	$N_2 + 3H_2 \rightleftharpoons 2NH_3$	-2	$K_p = K_c(RT)^{-2}$	$\frac{4x^4 v^2}{27(1-x)^4}$	$\frac{16x^2 (2-x)^2}{27(1-x)^4 p^2}$	$\text{L}^2 \text{mol}^{-2}$	atm <sup>-2</sup>	-ve (exothermic)	Low temperature Low pressure High concentration of reactant
7.	$PCl_5 + Cl_2 \rightleftharpoons PCl_3$	-1	$K_p = K_c(RT)^{-1}$	$\frac{xv}{(1-x)^2}$	$\frac{x(2-x)}{(1-x)^2} p$	$\text{L mol}^{-1}$	atm <sup>-1</sup>	-ve (exothermic)	Low temperature Low pressure High concentration of reactant
8.	$2SO_3 + O_2 \rightleftharpoons 2SO_2$	-1	$K_p = K_c(RT)^{-1}$	$\frac{x^2 v}{(1-x)^3}$	$\frac{x^2 (3-x)}{(1-x)^3} p$	$\text{L mol}^{-1}$	atm <sup>-1</sup>	-ve (exothermic)	Low temperature Low pressure High concentration of reactant



## SOLVED EXAMPLES

**Q.1** For the reaction  $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$ ,

The moles of each component  $\text{PCl}_5$ ,  $\text{PCl}_3$  and  $\text{Cl}_2$  at equilibrium were found to be 2. If the total pressure is 3 atm. The  $K_p$  will be –

- (A) 1 atm.                      (B) 2 atm.                      (C) 3 atm.                      (D) 1.5 atm.

**Ans.** A

**Sol.** Total Moles = 2 + 2 + 2 = 6

$$P_{\text{PCl}_3} = \frac{2}{6} \times 3, P_{\text{PCl}_5} = \frac{2}{6} \times 3, P_{\text{Cl}_2} = \frac{2}{6} \times 3$$

$$K_p = \frac{P_{\text{PCl}_3} \times P_{\text{Cl}_2}}{P_{\text{PCl}_5}} = \frac{1 \times 1}{1} = 1 \text{ atmosphere.}$$

**Q.2** For the reaction



The value of equilibrium constant is 9.0. The degree of dissociation of HI will be –

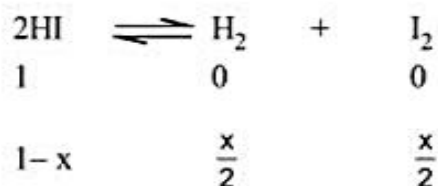
- (A) 2                      (B) 2/5                      (C) 5/2                      (D) 1/2

**Ans.** B

**Sol.** Equilibrium constant of the reaction



So the equilibrium constant for the dissociation of HI i.e.  $2\text{HI} \rightleftharpoons \text{H}_2 + \text{I}_2$  will be 1/9.



$$K_c = \frac{\frac{x}{2} \times \frac{x}{2}}{(1-x) \times (1-x)}$$

$$\frac{1}{9} = \frac{x^2}{2 \times 2(1-x)^2};$$

$$\frac{1}{3} = \frac{x}{2(1-x)}$$

or  $2 - 2x = 3x$

$$5x = 2$$

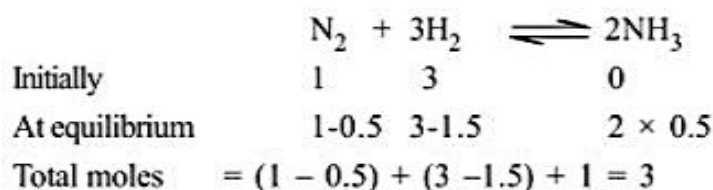
$$x = 2/5$$

**Q.3** For the reaction  $\text{N}_2 \rightleftharpoons 2\text{NH}_3$ ,  $\text{N}_2 : \text{H}_2$  were taken in the ratio of 1 : 3. Up to the point of equilibrium 50% each reactant has been reacted. If total pressure at equilibrium is P. The partial pressure of ammonia would be –

- (A) P/3                      (B) P/6                      (C) P/4                      (D) P/8

**Ans.** A

**Sol.**



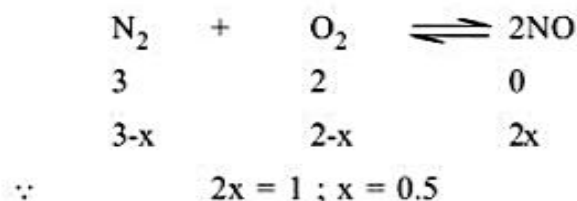
$$; P_{\text{NH}_3} = \frac{1}{3}P$$

**Q.4** In a reaction vessel of 2 litre capacity 3 moles of  $\text{N}_2$  reacts with 2 moles of  $\text{O}_2$  to produce 1 mole of NO. What is the molar concentration of  $\text{N}_2$  at equilibrium ?

- (A) 1.25                      (B) 1.50                      (C) 0.75                      (D) 2.0

**Ans.** A

**Sol.**



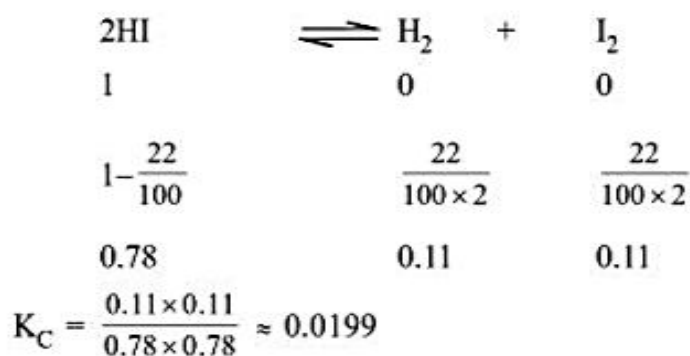
$$[\text{N}_2] = \frac{3-0.5}{2} = 1.25$$

**Q.5** HI was heated in a sealed tube at  $440^\circ\text{C}$  till the equilibrium was established. The dissociation of HI was found to be 22%. The equilibrium constant for dissociation is –

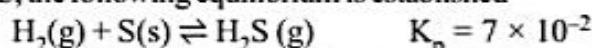
- (A) 0.282                      (B) 0.0786                      (C) 0.0199                      (D) 1.99

**Ans.** C

**Sol.** The equilibrium of the dissociation of



**Q.6** At 87°C, the following equilibrium is established



If 0.50 mole of hydrogen and 1.0 mole of sulphur are heated to 87°C in 1.0 L vessel, what will be the partial pressure of  $\text{H}_2\text{S}$  at equilibrium?

- (A) 0.966 atm (B) 1.38 atm (C) 0.0327 atm (D) 9.66 atm

**Ans.** A

**Sol.**  $\text{H}_2(\text{g}) + \text{S}(\text{s}) \rightleftharpoons \text{H}_2\text{S}(\text{g})$

Concentration at equilibrium  $0.5-x$   $-$   $x$

$$K_c = \frac{[\text{H}_2\text{S}]}{[\text{H}_2]} \Rightarrow 7 \times 10^{-2} = \frac{x}{0.5-x}$$

$$x = 0.0327$$

$$P_{\text{H}_2\text{S}} = \left( \frac{n_{\text{H}_2\text{S}}}{V} \right) RT \Rightarrow 0.0327 \times 0.0821 \times 360 \Rightarrow 0.966 \text{ atm. Ans.}$$

**Q.7** At some temperature  $\text{N}_2\text{O}_4$  is dissociated to 40% & 50% into  $\text{NO}_2$  at total pressure  $P_1$  &  $P_2$  atm respectively, then the ratio of  $P_1$  &  $P_2$  is

- (A)  $\frac{4}{5}$  (B)  $\frac{7}{4}$  (C)  $\frac{4}{7}$  (D) None of these

**Ans.** B

**Sol.**  $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$

at  $P_1$  (t=Eq)  $1-0.4$   $2(0.4)$   
 $= 0.6$   $= 0.8$

at  $P_2$  (t=Eq)  $1-0.5$   $2(0.5)$   
 $= 0.5$   $= 1$

$\therefore$  temperature is same,  $\therefore K_p$  is same

$$\frac{\left( \frac{0.8}{1.4} P_1 \right)^2}{\frac{0.6}{1.4} P_1} = \frac{\left( \frac{1}{1.5} P_2 \right)^2}{\left( \frac{0.5}{1.5} P_2 \right)} \Rightarrow \frac{P_1}{P_2} = \frac{1.4 \times 0.6}{(0.8)^2 \times 1.5 \times 0.5} = \frac{7}{4}$$

**Q.8**  $\Delta G^\circ$  for the dissociation of the dimer ( $\text{A}_2 \rightleftharpoons 2\text{A}$ ) in benzene solution at 27°C is 6.909 kcal/mol.

If 8 moles of A is dissolved in 10 dm<sup>3</sup> of benzene at 27°C. What is the ratio of equilibrium concentration of monomer to dimer ( $[\text{A}]/[\text{A}_2]$ )? **Given :**  $R = 2 \text{ Cal/mol.K}$

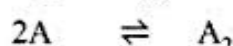
- (A) 1 : 200 (B) 1 : 100 (C) 200 : 1 (D) 800 : 1

**Ans.** A

**Sol.**  $\Delta G^\circ = -RT \ln K_{\text{eq}}$   
 $6.909 \times 1000 = -2 \times 300 \times 2.303 \log K_c$

$$-5 = \log K_c \text{ or } K_c = 10^{-5}$$

$$K_c' = 1/K_c = 10^5$$



$$0.8 - 2x \quad x$$

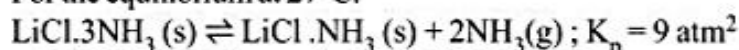
$$\because K'_C \text{ is very high} \quad \text{so } 2x \approx 0.8 \Rightarrow x \approx 0.4$$

$$\therefore 0.8 - 2x \approx y$$

$$10^5 = \frac{0.4}{(y)^2} \quad ; \quad y = (0.4 \times 10^{-5})^{1/2} \Rightarrow 2 \times 10^{-3}$$

$$\frac{[A]}{[A_2]} = \frac{y}{x} = \frac{2 \times 10^{-3}}{0.4} = \frac{5}{1000} = \frac{1}{200} \quad \text{Ans.}$$

**Q.9** For the equilibrium at 27°C.



A 24.63 litre flask contain 1 mol  $\text{LiCl} \cdot \text{NH}_3$ . How many moles of  $\text{NH}_3$  should be added to flask at this temperature to drive the backward reaction for completion.

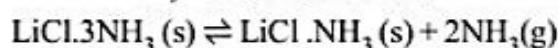
**Sol.**  $K_p = 9 \text{ atm}^2$

$$p_{\text{NH}_3}^2 = 9 \text{ atm}^2$$

$$p_{\text{NH}_3} = 3 \text{ atm}$$

$$3 \times 24.63 = n_{\text{NH}_3} \times R \times 300$$

$$n_{\text{NH}_3} = 3 \text{ (at equilibrium)}$$

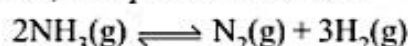


$$\begin{array}{ccc} 1 & & n \\ 0 & & n - 2 \end{array}$$

$$n - 2 = 3$$

$$n = 5 \text{ moles}$$

**Q.10** In a system, the equilibrium reaction :



was studied starting with  $\text{NH}_3$  and Ne (inert gas). It is found that at 10 atm and 700 K, the equilibrium gaseous mixture contains 10 mole % each of  $\text{NH}_3(\text{g})$  and Ne(g). Calculate  $K_p$  (in  $\text{atm}^2$ )

**Sol.**  $X_{\text{N}_2} + X_{\text{H}_2} = 1 - 0.1 - 0.1 = 0.8$

$$X_{\text{N}_2} = \frac{1}{4} \times 0.8 \Rightarrow 0.2$$

$$X_{\text{H}_2} = \frac{3}{4} \times 0.8 \Rightarrow 0.6$$

$$P_{\text{NH}_3} = 0.1 \times 10 = 1 \text{ atm}$$

$$P_{\text{N}_2} = 0.2 \times 10 = 2 \text{ atm}$$

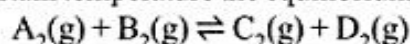
$$P_{\text{H}_2} = 0.6 \times 10 \Rightarrow 6 \text{ atm}$$

$$K_p = 2 \times 216$$

$$K_p = 432 (\text{atm})^2 \quad \text{Ans.}$$



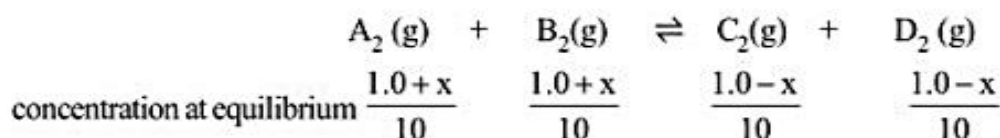
**Q.11** At a certain temperature the equilibrium constant  $K_c$  is 0.25 for the reaction



If we take 1 mole of each of the four gases in a 10 litre container, what would be equilibrium concentration of  $A_2(g)$ .

**Sol.**  $Q = \frac{1 \times 1}{1 \times 1} \Rightarrow 1$

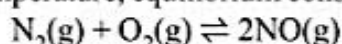
$\therefore Q > K_c$  so reaction will proceed in backward direction



$$0.25 = \frac{\left(\frac{1-x}{10}\right)^2}{\left(\frac{1+x}{10}\right)^2} \Rightarrow 0.5 = \frac{1-x}{1+x} \Rightarrow 0.5 + 0.5x = 1-x$$

$$1.5x = 0.5 \Rightarrow x = 0.333 \quad [A_2(g)] = \frac{1+x}{10} \Rightarrow \frac{1.333}{10} \Rightarrow 0.13 \text{ Ans.}$$

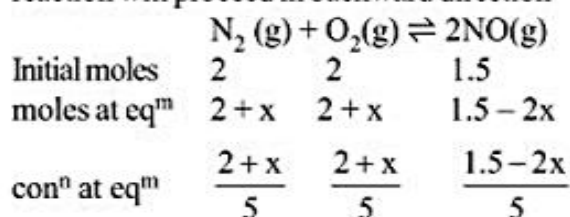
**Q.12** At a certain temperature, equilibrium constant  $K_c = 4 \times 10^{-2}$  for the reaction



If we take 1.5 mole of NO and 2 mole each of  $N_2$  &  $O_2$  in 5 litre vessel, what would be the equilibrium concentration of NO (in mole/litre)?

**Sol.**  $Q_c = \frac{(1.5/5)^2}{(2/5)^2} \Rightarrow 0.5625$  ;  $\therefore Q > K_c$

reaction will proceed in backward direction



$$K_c = \frac{[NO(g)]^2}{[N_2(g)][O_2(g)]} = \frac{\left(\frac{1.5-2x}{5}\right)^2}{\left(\frac{2+x}{5}\right)^2}$$

$$\frac{1.5-2x}{2+x} \Rightarrow \sqrt{0.04} \Rightarrow 0.2$$

$$1.5-2x = 0.4 + 0.2x \quad x = 0.5$$

$$\therefore \text{Equilibrium concentration of NO} = \frac{1.5-2x}{5} \Rightarrow 0.1 \text{ M Ans.}$$

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## IONIC EQUILIBRIUM

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### INTRODUCTION

Chemical reactions mostly take place in solutions. Solution chemistry plays a very significant role in chemistry. All chemical substances are made up of either polar units (called ions) or non-polar units. The behaviour of these substances depends upon their nature and conditions of the medium in which they are added. It is therefore necessary to understand the principles that govern their behaviour in solution.

Ionic equilibrium is observed in substances that undergo ionization easily, or in polar substances in which ionization can be induced. Ionic and polar substances are more easily soluble in polar solvents because of the ease of ionization taking place in the solvent medium. With the dissolution of ionic and polar substances in the solvent, these solutions become rich in mobile charge carriers (ions) and thus can conduct electricity. Substances, which are capable of conducting electricity are called **electrolytes** while those substances which are non-conducting are called **non-electrolytes**.

*The concepts and principles underlying chemical equilibrium are also applicable for ionic equilibrium. The fundamental concepts of chemical equilibrium, which are useful in ionic equilibrium are :*

- The equilibrium are dynamic in nature.
- The equilibrium constant is independent of the initial concentration of reactants.
- The equilibrium constant depends on temperature and nature of reactants and products.
- The equilibrium can be attained from either side.
- The concentration of pure solids, pure liquids and solvents do not appear in the equilibrium constant expression.
- The equilibrium in solutions will only have equilibrium constant.
- The degree of dissociation of a weak electrolyte is the fraction of a mole of electrolyte that underwent dissociation.
- The equilibrium constant for the overall reaction is given by the product of the equilibrium constant of the individual reactions
- In order to predict the direction of equilibrium movement, reaction quotient (Q) should be compared with equilibrium constant, K. If  $Q = K$ , reaction is at equilibrium, if  $Q < K$ , reaction will move from right to left to attain equilibrium.
- According to Le Chatelier principle if an external stress is applied to a system at equilibrium, the system will adjust to partially offset the stress.

### IMPORTANT TERMS

#### Electric conductivity

Substance which allow the electric current to pass through them are called electric conductors and this property is called electric conductivity.

On the basis of Electric conductivity, substances are of two types :

#### 1 Non conductors :

Substance which do not allow the electric current to pass through are called nonconductors. eg. All covalent compounds & nonmetals.

#### 2 Conductors :

Substance which allow the electric current to pass through are called conductors. eg. all metals, alloys, all acid and bases, salt and graphite etc.

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On the basis of conducting units conductors are of two types :

**Metallic or Electric Conductors :**

Electricity conduct due to the presence of free and mobile electron which act as electricity conducting unit called metallic or electric conductors. eg. Metals, Alloys, Graphite, Gas, Carbon etc.

**Ionic Conductors or Electrolytes :**

Conductors in which the current is passes through due to the presence of free ions are called Ionic Conductors or Electrolyte or Electrolytic conductors.

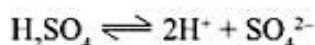
**Ionisation :**

The process in which molecules of acids bases and salts when melted or dissolve in water dissociate into ions is called ionization.

**ARRHENIUS THEORY OF ELECTROLYTIC DISSOCIATION**

*The compounds which give ions either in molten state or in solution are called electrolytes. In the solid state they are bad conductors, but become good conductors either in the molten state in solution.*

- (i) When an electrolyte is dissolved in a solvent (usually water) or is melted by heating, it spontaneously dissociates into oppositely charged particles called ions, to a considerable extent.



The positively charged ions are called cations and the negatively charged ions are called anions.

- (ii) Since the solution of an electrolyte, as a whole, is electrically neutral, i.e; the total charge on the cations is equal to the total charge on the anions.
- (iii) Electrolytic dissociation or ionization produces equilibrium between unionized molecules and the ions in solution. The degree of dissociation of an electrolyte ( $\alpha$ ) is the fraction of one mole of an electrolyte that has dissociated under the given conditions.

The value of  $\alpha$  depends on

- |                                   |                               |
|-----------------------------------|-------------------------------|
| (a) the nature of the electrolyte | (b) the nature of the solvent |
| (c) the dilution and              | (d) the temperature           |

- (a) **Nature of electrolyte :** Some electrolyte, e.g., mineral acid such as  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$  and  $\text{HNO}_3$ , alkalis such as  $\text{NaOH}$  and  $\text{KOH}$  and all salts have a very high degree of ionization ( $\approx 1$ ) at all reasonable concentration. They are known as strong electrolytes. The number of ions of strong electrolytes is large and thus such solutions have high conductance.

Some electrolytes, e.g., organic acids such as acetic acid and bases like ammonium hydroxide have a low degree of ionization in solution. They are called weak electrolytes. The number of ions in solutions of weak electrolytes is quite small and thus such solutions have low conductance.

- (b) **Nature of the solvent :** A solvent which has a high dielectric constant weakens the attractive force between the cations and anions. Hence a solvent of high dielectric constant favours the dissociation of the electrolyte.



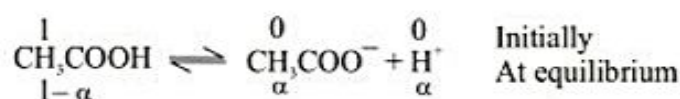
Likewise a solvent which can solvate the ions readily, and can release energy by solvation, favours the dissociation of the electrolyte. Thus the dissociation of acids in water is favoured by the hydration of the hydrogen ions to form hydronium ions. The enthalpy of hydration of the proton has a very high value.

- (c) **Dilution** : For some electrolytes, degree of dissociation increases with dilution as explained by Ostwald's dilution law (explained later)
- (d) **Temperature** : Increase of temperature generally increases ionization.

## TYPES OF ELECTROLYTES

There are two types of electrolytes:

- (1) **Strong electrolytes** : These electrolytes are almost completely ionized when dissolved in a polar medium like water. In solution they are excellent conductors, e.g.,  $\text{HNO}_3$ ,  $\text{HCl}$ ,  $\text{KOH}$ ,  $\text{NaOH}$ , etc. Their degree of ionization is high and approaches unity.
- (2) **Weak electrolytes** : These are not completely ionized when dissolved in a polar solvent and they behave as poor conductors of electricity, e.g.,  $\text{CH}_3\text{COOH}$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{H}_3\text{BO}_3$ ,  $\text{NH}_4\text{OH}$ , etc., Equilibrium between ions and unionized molecules is established in solution, e.g.,



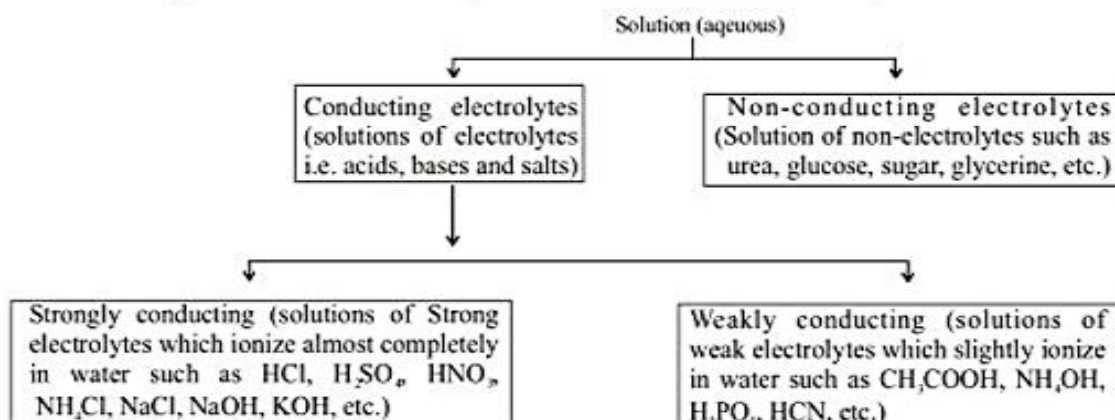
The above equilibrium is termed as ionic equilibrium. Degree of ionization of weak electrolytes is much less than unity. ( $\alpha \ll 1$ )

Degree of ionization, may be defined as a fraction of total number of molecules of an electrolyte which dissociate into ions.

$$\alpha = \frac{\% \text{ ionization}}{100}$$

$$\text{Degree of Ionization } (\alpha) = \frac{\text{Number of mole dissociated}}{\text{Total number of moles taken}}$$

The following classification of electrolytes is based on their behaviour in a particular solvent, i.e., water.





**Note :** - Electrolyte may behave as a strong one in aqueous solution, but it may behave as a weak one in another solvent. For example, sodium chloride behaves as a strong electrolyte and acetic acid as a weak electrolyte when dissolved in water but their conducting abilities are comparable in liquid ammonia solvent.

### Illustration

1. Identify the non-electrolyte, strong electrolyte and weak electrolytes in aq. medium of the following substance.

NaOH, HCl, NaCl,  $\text{NH}_2\text{CONH}_2$  (Urea),  $\text{H}_2\text{SO}_4$ ,  $\text{H}_3\text{PO}_4$ , HCN,  $\text{NH}_4\text{OH}$ , KOH,  $\text{C}_2\text{H}_5\text{COOH}$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{HNO}_3$ ,  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$  (Sugar),  $\text{C}_6\text{H}_{12}\text{O}_6$  (glucose)

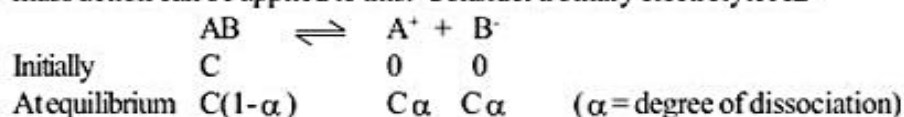
**Sol.** Non-electrolyte :  $\text{NH}_2\text{CONH}_2$ ,  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ,  $\text{C}_6\text{H}_{12}\text{O}_6$

Weak-Electrolyte :  $\text{H}_3\text{PO}_4$ , HCN,  $\text{NH}_4\text{OH}$ ,  $\text{C}_2\text{H}_5\text{COOH}$

Strong-Electrolyte : NaOH, HCl, NaCl,  $\text{H}_2\text{SO}_4$ , KOH,  $\text{NH}_4\text{Cl}$ ,  $\text{HNO}_3$

### OSTWALD'S DILUTION LAW

The application of law of mass action to weak electrolytes is known as Ostwald dilution law. There exists dynamic equilibrium between ions and undissociated molecules of the electrolytes in solution and law of mass action can be applied to this. Consider a binary electrolyte AB



$$K = \frac{[\text{A}^+][\text{B}^-]}{[\text{AB}]} = \frac{\text{C}\alpha\text{C}\alpha}{\text{C}(1-\alpha)} = \frac{\text{C}\alpha^2}{(1-\alpha)}$$

K is termed as ionization constant. For a weak electrolyte value of  $\alpha$  is very-very small compared to 1 and  $(1-\alpha) \approx 1$

$$\therefore K = \text{C}\alpha^2 \Rightarrow \alpha = \sqrt{\frac{K}{\text{C}}} \Rightarrow \alpha \propto \frac{1}{\sqrt{\text{C}}}$$

If V be the volume of the solution containing 1 mole of the solute  $\text{C} = \frac{1}{V}$ .

- Hence  $\alpha = \sqrt{KV}$  or  $\alpha \propto \sqrt{V}$  as ionic equilibrium is set up in case of weak electrolytes.
- Ostwald's dilution is applicable only in case of weak electrolytes.
- The approximation  $(1-\alpha) \approx 1$  can be applied only if  $\alpha < 5\%$ . If on solving a problem by applying the approximate formula  $\alpha$  comes out to be  $> 5\%$  the problems may be solved by applying exact formula and  $\alpha$  may be calculated applying solution of quadratic equation

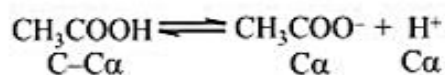
$$\alpha = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \quad (\text{for, } a\alpha^2 + b\alpha + c = 0)$$

**Illustration**

1. What concentration of acetic acid is needed to give a hydrogen ion concentration of  $3.5 \times 10^{-4}$  M? ( $K_a = 1.8 \times 10^{-5}$ )  
 (A)  $3.5 \times 10^{-4}$  M (B)  $6.80 \times 10^{-3}$  M (C)  $4.2 \times 10^{-4}$  M (D)  $7.2 \times 10^{-4}$  M

Ans. (B)

Sol. Let the concentration of acetic acid be 'C'.



$$K_a = 1.8 \times 10^{-5} = \frac{C\alpha \cdot C\alpha}{C(1-\alpha)} = C\alpha^2$$

$$\text{Now } \alpha^2 = \frac{K_a}{C} \text{ or } \alpha = \sqrt{\frac{K_a}{C}} \text{ or } C\alpha = \sqrt{K_a \cdot C}$$

$$C\alpha = [\text{H}^+] = 3.5 \times 10^{-4} \text{ M} \quad \therefore 3.5 \times 10^{-4} = \sqrt{1.8 \times 10^{-5} C}$$

$$\text{Or } \sqrt{C} = \frac{3.5 \times 10^{-4}}{\sqrt{1.8 \times 10^{-5}}} \text{ or } C = \frac{(3.5 \times 10^{-4})^2}{1.8 \times 10^{-5}} = \frac{12.25 \times 10^{-8}}{1.8 \times 10^{-5}} = 6.80 \times 10^{-3} \text{ mol L}^{-1}$$

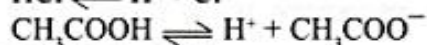
**Exercise**

1. Calculate the concentration of  $\text{C}_2\text{H}_5\text{COOH}$  that is needed to give a hydrogen ion concentration of  $10^{-4}$  M? ( $K_a = 2 \times 10^{-6}$ )  
 Ans.  $5 \times 10^{-3}$  M

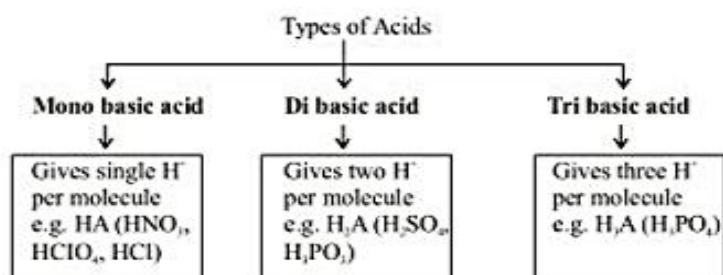
**Limitations of Ostwald's dilution law :** It holds good only for weak electrolytes and fails completely in the case of strong electrolytes

**CONCEPT OF ACIDS AND BASES****(A) The Arrhenius concept****Arrhenius acid :**

An acid is a substance which gives hydrogen ions in aqueous solution as the only cations. e.g.,



Ex.  $\text{HNO}_3$ ,  $\text{HClO}_4$ ,  $\text{HCl}$ ,  $\text{HI}$ ,  $\text{HBr}$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{H}_3\text{PO}_4$  etc.

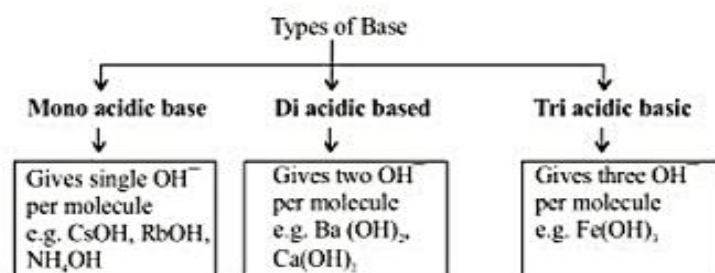
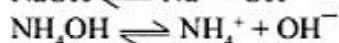
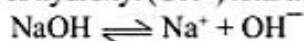
**Note :**

- H<sub>3</sub>BO<sub>3</sub> is not an Arrhenius acid.
- H<sup>+</sup> ion in water is extremely hydrated (in form of H<sub>3</sub>O<sup>+</sup>, H<sub>5</sub>O<sub>2</sub><sup>+</sup>, H<sub>7</sub>O<sub>3</sub><sup>+</sup>)
- The structure of solid HClO<sub>4</sub> is studied by X-ray, It is found to be consisting of H<sub>3</sub>O<sup>+</sup> and ClO<sub>4</sub><sup>-</sup>  

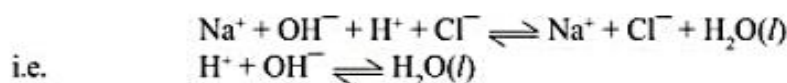
$$\text{HClO}_4 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{ClO}_4^- \text{ (Better representation)}$$

**Arrhenius base :**

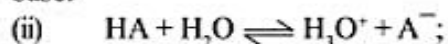
A base is a substance which gives hydroxyl (OH<sup>-</sup>) ions in a aqueous solution as the only anions.

**Note :**

- OH<sup>-</sup> ion is present also in hydrated form of H<sub>3</sub>O<sub>2</sub><sup>-</sup>, H<sub>7</sub>O<sub>4</sub><sup>-</sup>, H<sub>5</sub>O<sub>3</sub><sup>-</sup>
- First group elements (except Li) form strong bases
- Neutralization is the combination of H<sup>+</sup> ions of the acid and OH<sup>-</sup> ions of the base to form unionized water.

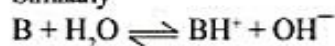
**Strength of acid or base :**

(i) Strength of acid or base depends on the extent of its ionisation. Hence equilibrium constant K<sub>a</sub> or K<sub>b</sub>, respectively of the following equilibria gives a quantitative measurement of the strength of the acid or base.



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

(iii) Similarly

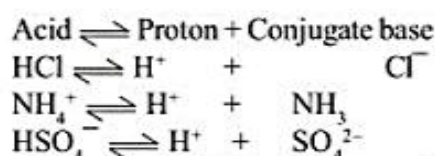


$$K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]}$$

Here H<sub>2</sub>O is solvent.

### (B) The Bronsted-Lowry theory (Protonic concept)

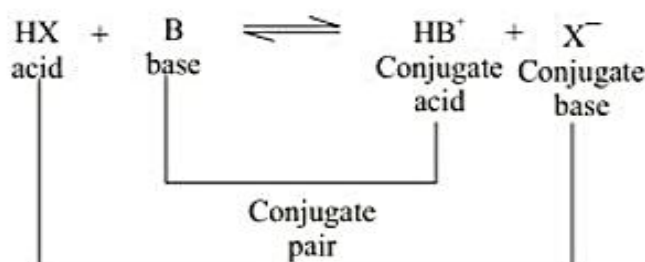
According to this concept, an acid is a substance which has tendency to lose a proton ( $H^+$ ), i.e. an acid is a proton donor and a base is a substance, which has a tendency to accept a proton, i.e., it is a proton acceptor. When an acid loses a proton, the residue will have a tendency to regain a proton and hence it is referred as conjugate base



The acid and the conjugate base, which differ by a proton, forms a conjugate pair. For example, HCl and  $\text{Cl}^-$  ions form a conjugate pair,  $\text{Cl}^-$  is the conjugate base of HCl and HCl is the conjugate acid of  $\text{Cl}^-$ . From the examples given above, it is clear that acids and bases may be molecules or ions, but at least one of the members of a conjugate pair should be an ion.

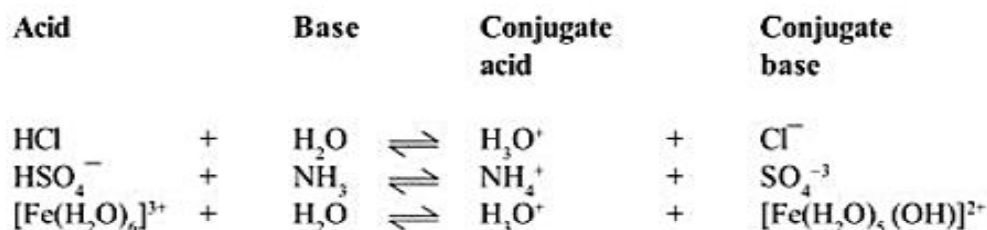
#### Conjugate acid–base pairs

In a typical acid base reaction



\* Forward reaction – Here HX being a proton donor is an acid  
B being a proton acceptor is a base

Backward reaction – Here  $\text{HB}^+$  being a proton donor is an acid  
 $\text{X}^-$  being a proton acceptor is a base



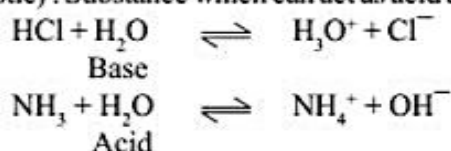
#### Note :

- Conjugate acid - base pair differ by only one proton.
- Strong acid will have weak conjugate base and vice versa.
- Reaction will always proceed from strong acid to weak acid or from strong base to weak base.



	Acid	Conjugate base	Base	Conjugate acid
Ex.	HCl	$\text{Cl}^-$	$\text{NH}_3$	$\text{NH}_4^+$
	$\text{H}_2\text{SO}_4$	$\text{HSO}_4^-$	$\text{H}_2\text{O}$	$\text{H}_3\text{O}^+$
	$\text{HSO}_4^-$	$\text{SO}_4^{2-}$	$\text{RNH}_2$	$\text{RNH}_3^+$
	$\text{H}_2\text{O}$	$\text{OH}^-$		

Amphoteric (amphiprotic) : Substance which can act as acid as well as base are known as amphoteric



### Behaviour of acids and bases in aqueous solution

- (i) **Acids in water :** Water functions as a weak base and accepts a proton from the acid, thus



$\text{A}^-$  can be considered as the conjugate base of anion of salt of the acid HA. So an aqueous solution of an acid contains hydronium ( $\text{H}_3\text{O}^+$ ) ions (and not  $\text{H}^+$  ions)

- (ii) **Strong and Weak acids :** (Relationship between a conjugate pair). An acid is considered to be a strong acid, it can give up its proton readily. In an aqueous solution of HCl, there is equilibrium



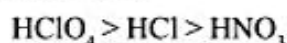
Since HCl can give up its proton readily, this equilibrium will lie far to the right. Consequently the base  $\text{Cl}^-$  cannot take up the proton from  $\text{H}_3\text{O}^+$  readily, i.e.,  $\text{Cl}^-$  is a weak base. In general, the conjugate base of a strong acid will be a weak base.

In the case of a weak acid like phenol,



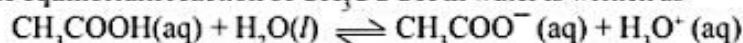
The equilibrium will lie far to the left. So the conjugate base ( $\text{C}_6\text{H}_5\text{O}^-$ ) of a weak acid ( $\text{C}_6\text{H}_5\text{OH}$ ) will be moderately strong. Again there is little ionization in the aqueous solution of a weak acid so the acid is a weak electrolyte and the solution has a low conductance.

Based on studies of acids it is established that,



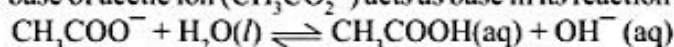
- (iii) Relationship between the ionization constants of acids and their conjugate bases

Let us derive a relationship between the ionization constants of acid,  $\text{CH}_3\text{COOH}$  and its conjugate  $\text{CH}_3\text{COO}^-$ . The equilibrium reaction of  $\text{CH}_3\text{COOH}$  in water is written as



$$K_{\text{eq}} [\text{H}_2\text{O}] = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]} = K_{\text{a}} \quad \text{.....(i)}$$

The conjugate base of acetic ion ( $\text{CH}_3\text{CO}_2^-$ ) acts as base in its reaction with water as



$$K'_{\text{eq}} [\text{H}_2\text{O}] = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} = K_{\text{b}}$$

$$[\text{OH}^-] = \frac{K_w}{[\text{H}^+]} \quad \text{.....(ii)}$$

$$\therefore K_b = \frac{[\text{CH}_3\text{COOH}] K_w}{[\text{CH}_3\text{COO}^-][\text{H}^+]}$$

$$K_b = \frac{K_w}{K_a}$$

Thus, stronger the acid (the larger  $K_a$ ), weaker will be its conjugate base (the smaller  $K_b$ ) and vice versa. Therefore, for an acid-conjugate base pair.

$$K_w = K_a \times K_b$$

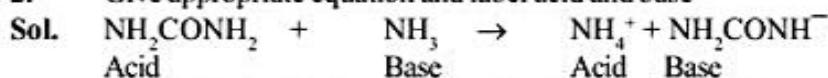
### Illustration

1. Which is the strongest Bronsted base in the following anion-  
(A)  $\text{ClO}^-$  (B)  $\text{ClO}_2^-$  (C)  $\text{ClO}_3^-$  (D)  $\text{ClO}_4^-$

Ans. (A)

Sol.  $\text{HClO}$  is weakest acid among  $\text{HClO}$ ,  $\text{HClO}_2$ ,  $\text{HClO}_3$  and  $\text{HClO}_4$

2. Give appropriate equation and label acid and base-



In liquid  $\text{NH}_3$  solution urea can show weak acidic nature, while in water urea does not dissociate

### Exercise

1. Ammonium ion is-  
(A) A Lewis acid (B) Lewis base (C) Bronsted acid (D) Bronsted base

Ans. (C)

2. (a) Write conjugate acids of  $\text{SO}_4^{2-}$ ,  $\text{NH}_2^-$ ,  $\text{F}^-$   
 (b) Write conjugate base of  $\text{HNO}_2$ ,  $\text{H}_2\text{CO}_3$ ,  $\text{HClO}_4$   
 (c) Write conjugate acids and conjugate base of amphoteric species  
 $\text{HS}^-$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{HSO}_4^-$

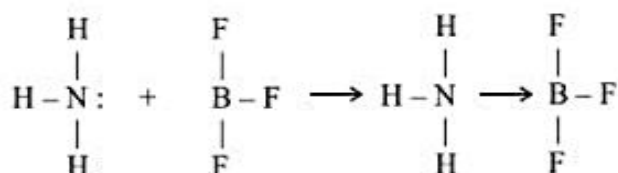
Ans. (a)  $\text{HSO}_4^-$ ,  $\text{NH}_3$ ,  $\text{HF}$   
 (b)  $\text{NO}_2^-$ ,  $\text{HCO}_3^-$ ,  $\text{ClO}_4^-$   
 (c)  $(\text{H}_2\text{S}, \text{S}^{2-})$   $(\text{NH}_4^+, \text{NH}_2^-)$   $(\text{H}_2\text{SO}_4, \text{SO}_4^{2-})$

3. Which of the following is the strongest base-  
(A)  $\text{NH}_2^-$  (B)  $\text{CH}_3\text{COO}^-$  (C)  $\text{C}_2\text{H}_5\text{O}^-$  (D)  $\text{OH}^-$

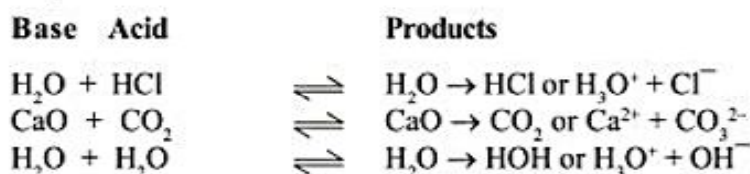
Ans. (A)

**(C) Lewis Electronic theory**

According to this theory an acid is a molecule or ion, which can accept an electron pair with the formation of a coordinate bond. For example, in  $\text{BF}_3$  the boron atom can accept a pair of electron; so  $\text{BF}_3$  is a Lewis acid. A base must therefore be any molecule or ions, which has a lone pair of electron, which it can donate. For example, ammonia molecule has a lone pair of electron; so it is a Lewis base.



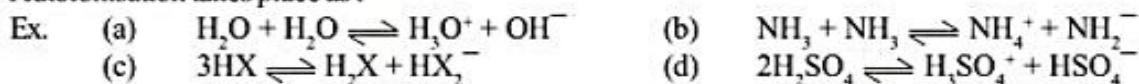
Other examples of Lewis acid-base neutralization

**Classification of Solvents :**

There are two types of solvents : (i) Protionic (protic) and (ii) Aprotic

**(i) Protionic or protic solvent**

- (a) They are characterized by the presence of a transferable hydrogen and the formation of "Onium" ions. Autoionisation takes place as :



- (b) Protionic solvents may be

- (a) Acidic (Anhydrous sulphuric acid, liquid HF, Glacial acetic acid etc.)  
 (b) Basic (liquid  $\text{NH}_3$ )  
 (c) Amphiprotic ( $\text{H}_2\text{O}$ , proton containing anions)

**(c) Aprotic solvents :**

Such solvents do not have replaceable hydrogen ion in them. These can be classified into three categories.

- (a) Non polar or very weakly polar, nondissociated liquids, which do not solvate strongly.

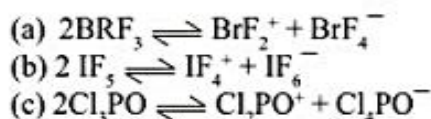
Ex.  $\text{CCl}_4$ , hydrocarbons,  $\text{C}_6\text{H}_6$ ,  $\text{C}_6\text{H}_{12}$  etc.

- (b) Non-ionised but strongly solvating, generally polar solvents.

Ex. Acetonitrile  $\text{CH}_3\text{CN}$ , DMSO (dimethyl sulfoxide), THF (Tetra hydro furan) and  $\text{SO}_2$ .

- (c) Highly polar, autoionising solvents.

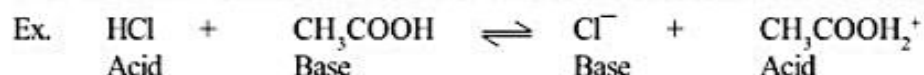
Ex. Inter halogen compounds ( $\text{BrF}$ ,  $\text{IF}_3$  and trichloro phosphine)





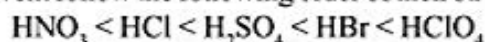
## LEVELLING SOLVENTS

- (i) The Bronsted - Lowry theory can be extended to acid-base reactions in non-aqueous solvents. It can be used in differentiating the acid strength of a particular acid and in titration of weak bases.
- (ii) In water solvent, mineral acids appear to be equally strong because of their complete ionisation, so water is called levelling solvent because it levels all the acids to the same strength.
- (iii) If instead of water solvent, we take mineral acids in pure acetic acid solvent (which is poor proton acceptor as compared to water) it is found acids become weak and can be differentiated.



In above example acetic acid and  $\text{Cl}^-$  ions both compete for protons and the former being a poor proton acceptor does it much less effectively than water. Thus HCl in acetic acid solvent appears to be a much weaker acid than that in water.

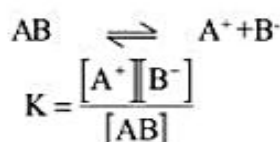
- (iv) Mineral acids in acetic acid solvent follow the following order of their strengths.



## COMMON ION EFFECT

The degree of dissociation of a weak electrolyte is suppressed by the addition of another electrolyte (strong) containing common ion. This is referred to as common ion effect e.g. Acetic acid is a weak electrolyte and its ionization is suppressed in presence of strong acid ( $\text{H}^+$  ion as common ion).

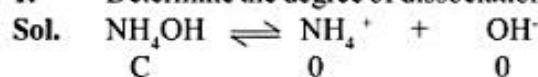
Let AB be the weak electrolyte, considering its dissociation



The equilibrium constant K has a definite value at a given temperature. If another electrolyte containing  $\text{A}^+$  or  $\text{B}^-$  ions added to the above solution will increase the concentration of  $\text{A}^+$  or  $\text{B}^-$  ions, in order, that K remain constant, the concentration of AB must increase, equilibrium will shift to the left side.

### Illustration

1. Determine the degree of dissociation of 0.05 M  $\text{NH}_3$  at  $25^\circ\text{C}$  in a solution of  $\text{pH} = 11$



Given  $\text{pH} = 11 \therefore [\text{H}^+] = 10^{-11}$

$$[\text{H}^+][\text{OH}^-] = 1 \times 10^{-14}$$

$$\therefore [\text{OH}^-] = \frac{1 \times 10^{-14}}{10^{-11}} = 10^{-3} = C\alpha$$

$$\therefore \alpha = \frac{[\text{OH}^-]}{C} = \frac{10^{-3}}{0.05} = 2 \times 10^{-2} \text{ or } 0.2\%$$



2. What will be the resultant pH when 200 ml of an aqueous solution of HCl (pH=2.0) is mixed with 300 ml of an aqueous solution of NaOH (pH=12.0)

**Sol.** pH of HCl = 2,  $\therefore [\text{HCl}] = 10^{-2} \text{ M}$

pH of NaOH = 12, pOH = 2  $\therefore [\text{NaOH}] = 10^{-2} \text{ M}$

	HCl	+	NaOH	$\rightarrow$	NaCl	+	H <sub>2</sub> O
Meq. initial	200x10 <sup>-2</sup>		300x10 <sup>-2</sup>		0		0
	=2		=3				
Meq. final	0		1		2		2

$$\therefore [\text{OH}^-] \text{ from NaOH} = \frac{1}{500} = 2 \times 10^{-3} \text{ M}$$

$$\text{pOH} = -\log[\text{OH}^-] = -\log(2 \times 10^{-3})$$

$$\therefore \text{pOH} = 2.6989$$

$$\therefore \text{pH} = 14 - \text{pOH} = 14 - 2.6989 = 11.3010.$$

3.  $K_a$  for acid HA is  $4.9 \times 10^{-8}$ . After making the necessary approximation, calculate for its decimolar solution at 25°C.

(i) % dissociation      (ii) pH      (iii) OH<sup>-</sup> concentration

**Sol.**  $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$   
C                      0                      0

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \Rightarrow K_a = \frac{C\alpha \cdot C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)} \approx C\alpha^2$$

$$\text{i) } \therefore \alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{4.9 \times 10^{-8}}{1/10}} \quad (C = 1/10 \text{ M})$$

$$= 7 \times 10^{-4} = 0.07 \%$$

$$\text{ii) } [\text{H}^+] = C\alpha = \frac{1}{10} \times 7 \times 10^{-4} = 7 \times 10^{-5} \text{ mol L}^{-1}$$

$$\text{iii) } [\text{H}^+][\text{OH}^-] = 1 \times 10^{-14}$$

$$\therefore [\text{OH}^-] = \frac{10^{-14}}{7 \times 10^{-5}} = 1.43 \times 10^{-10} \text{ mol / Lt.}$$

4. A solution of HCl has a pH = 5. If one ml of it is diluted to 1 liter what will be pH of resulting solution?

**Sol.**  $[\text{HCl}] = 10^{-5} \text{ M}$  (As pH = 5)

$$\text{Meq of HCl in 1 ml} = 10^{-5} \times 1 = 10^{-5}$$

Let normality after diluting

One ml of HCl (pH=5) to one liter is (N)

Meq of HCl (conc) = Meq of HCl dilute.

$$10^{-5} \times 1 = N \times 100 \Rightarrow N_{\text{HCl (dil.)}} = 10^{-8}$$



$$10^{-8} \quad 0 \quad 0 \quad \text{Initial}$$

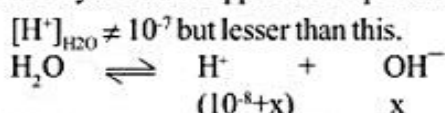
$$0 \quad 10^{-8} \quad 10^{-8} \quad \text{Final}$$

$\therefore [H^+] = 10^{-8}$  but  $pH = 8$  is not possible because solution is acidic. As  $(H^+) = 10^{-7} M$  are already present in solution from the dissociation of water and since  $10^{-8} < 10^{-7}$  and thus it should not be neglected

$$\therefore [H^+] = 10^{-8} + 10^{-7} = (1.1) \times 10^{-7} M$$

$$\therefore pH = 6.9586.$$

The above solution for pH of the resultant solution has discrepancy, that dissociation of weak electrolyte is also suppressed in presence of HCl due to common ion effect.



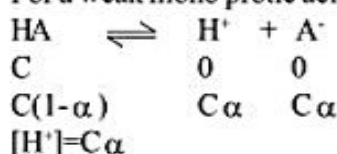
$$K_w = (10^{-8} + x)x \Rightarrow x = 0.95 \times 10^{-7}$$

$$\therefore [H^+] = 10^{-8} + 0.95 \times 10^{-7} = 21.05 \times 10^{-8}$$

$$\therefore pH = 6.9788$$

5. Prove that degree of dissociation of weak acid is given by  $\alpha = \frac{1}{1 + 10^{(pK_a - pH)}}$ . Where  $K_a$  is its dissociation constant of weak acid?

**Sol.** For a weak mono protic acid



$$K_a = \frac{C\alpha^2}{(1-\alpha)} \quad (\text{Ostwall dilution law})$$

$$\therefore C = \frac{K_a(1-\alpha)}{\alpha^2}$$

$$\therefore [H^+] = \frac{K_a(1-\alpha)}{\alpha^2} \times \alpha = \frac{K_a(1-\alpha)}{\alpha}$$

$$\Rightarrow -\log[H^+] = -[\log K_a + \log(1-\alpha) - \log \alpha]$$

$$\Rightarrow pH = -\log K_a + \log \frac{\alpha}{(1-\alpha)} \Rightarrow pH = pK_a - \log \frac{(1-\alpha)}{\alpha}$$

$$\Rightarrow \log \frac{(1-\alpha)}{\alpha} = (pK_a - pH) \Rightarrow \frac{(1-\alpha)}{\alpha} = 10^{(pK_a - pH)} \Rightarrow \frac{1}{\alpha} - 1 = 10^{(pK_a - pH)}$$

$$\Rightarrow \alpha = \frac{1}{1 + 10^{(pK_a - pH)}}$$

## PROPERTIES OF WATER

### Amphoteric (amphiprotic) Acid /Base nature :

Water act as an acid as well as a base according to Bronsted - Lowry theory but according to Lewis concept it can only be taken as base only.

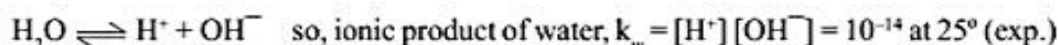
In pure water  $[H^+] = [OH^-]$  so it is neutral.

### Molar concentration / Molarity of water :

$$\text{Molarity} = \text{No. of moles/litre} = \frac{1000\text{g / litre}}{18\text{g / moles}} = 55.55 \text{ moles / litre} = 55.55 \text{ M (density} = 1 \text{ g/cc)}$$

### Ionic product of water :

According to arrhenius concept



Dissociation of water is endothermic, so on increasing temperature  $K_w$  increase.

$K_w$  increases with increase in temperature.

Now  $pH = -\log [H^+] = 7$  and  $pOH = -\log [OH^-] = 7$  for water at  $25^\circ\text{C}$  (experimental)

$$\left. \begin{array}{l} pH = 7 = pOH \Rightarrow \text{neutral} \\ pH < 7 \text{ or } pOH > 7 \Rightarrow \text{acidic} \\ pH > 7 \text{ or } pOH < 7 \Rightarrow \text{basic} \end{array} \right\} \text{ at } 25^\circ\text{C}$$

Ionic product of water is always a constant whatever has been dissolved in water since its an equilibrium constant so will be dependent only on temperature.

### Degree of dissociation of water :

$$\begin{aligned} H_2O \rightleftharpoons H^+ + OH^- \Rightarrow \alpha &= \frac{\text{no. of moles dissociated}}{\text{Total no. of moles initially taken}} \\ &= \frac{10^{-7}}{55.55} = 18 \times 10^{-10} \text{ or } 1.8 \times 10^{-7} \% \end{aligned}$$

### Absolute dissociation constant of water :

$$H_2O \rightleftharpoons H^+ + OH^- \quad K_a = K_b = \frac{[H^+][OH^-]}{[H_2O]} = \frac{10^{-7} \times 10^{-7}}{55.55} = 1.8 \times 10^{-16}$$

$$\text{So, } pK_a = pK_b = -\log (1.8 \times 10^{-16}) = 16 - \log 1.8 = 15.74$$

### Acidity and pH scale :

Acidic strength means the tendency of an acid to give  $H_3O^+$  or  $H^+$  ions in water.

So greater the tendency to give  $H^+$ , more will be the acidic strength of the substance.

Basic strength means to give  $OH^-$  ions, more will be basic strength of the substance.

The concentration of  $H^+$  ions is written in a simplified form introduced by Sorenson known as pH scale.

pH is defined as negative logarithm of activity of  $H^+$  ions.

$$\therefore \text{pH} = -\log a_{\text{H}^+} \quad (\text{where } a_{\text{H}^+} \text{, is the activity of H}^+ \text{ ions})$$

Activity of  $\text{H}^+$  ions is the concentration of free  $\text{H}^+$  ions or  $\text{H}_3\text{O}^+$  ions in a solution.

The pH scale was marked from 0 to 14 with central point at 7 at  $25^\circ\text{C}$ , taking water as solvent.

If the temperature and the solvent are changed, the pH range of the scale will also change. For example

0 – 14	at $25^\circ\text{C}$ ( $K_w = 10^{-14}$ )	Neutral point, pH = 7
0 – 14	at $80^\circ\text{C}$ ( $K_w = 10^{-13}$ )	Neutral point, pH = 6.5

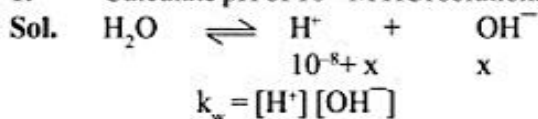
## pH CALCULATION OF DIFFERENT TYPES OF SOLUTIONS

### (a) Strong acid solution :

- If concentration is greater than  $10^{-6}\text{ M}$ .  
In this case  $\text{H}^+$  ions coming from water can be neglected.  
so  $[\text{H}^+] = \text{normality of strong acid solution.}$
- If concentration is less than  $10^{-6}\text{ M}$  but greater than  $10^{-8}\text{ M}$   
In this case  $\text{H}^+$  ions coming from water cannot be neglect.  
So  $[\text{H}^+] = \text{normality of strong acid} + \text{H}^+ \text{ ions coming from water in presence of this strong acid.}$
- If concentration is less than  $10^{-8}\text{ M}$ , in this case  $\text{H}^+$  ions coming from water is considered only.

### Illustration

1. Calculate pH of  $10^{-8}\text{ M HCl}$  solution.



$$10^{-14} = x(x + 10^{-8})$$

$$\Rightarrow x^2 + x \times 10^{-8} - 10^{-14} = 0$$

$$x = \frac{-10^{-8} \pm \sqrt{10^{-16} + 4 \times 10^{-14}}}{2} = \frac{-10^{-8} + 10^{-7} \sqrt{4 + \frac{1}{100}}}{2} = \frac{(\sqrt{401} - 1)10^{-8}}{2} = 0.95 \times 10^{-7}$$

$$[\text{H}^+] = 10.5 \times 10^{-8} = 1.05 \times 10^{-7}$$

$$\text{pH} = -\log [\text{H}^+]$$

$$\text{pH} = 7 - \log 1.05 \approx 7$$

### Exercise

1. Calculate pH of  $10^{-10}\text{ M HCl}$  solution.

Ans.  $\text{pH} \approx 7$



**(b) Strong base solution :**

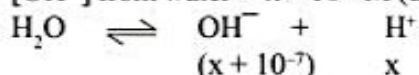
Calculate the  $[\text{OH}^-]$  which will be equal to normality of the strong base solution and then use  $K_w = [\text{H}^+] \times [\text{OH}^-] = 10^{-14}$ , to calculate  $[\text{H}^+]$

**Illustration**

1. Calculate pH of  $10^{-7}$  M of NaOH solution

Sol.  $[\text{OH}^-]$  from NaOH =  $10^{-7}$

$[\text{OH}^-]$  from water =  $x < 10^{-7}$  M (due to common ion effect)



$$K_w = [\text{H}^+] [\text{OH}^-] = 10^{-14} = x (x + 10^{-7})$$

$$x^2 + 10^{-7}x - 10^{-14} = 0$$

$$\Rightarrow x = \frac{\sqrt{5}-1}{2} \times 10^{-7} = 0.618 \times 10^{-7} \quad (\sqrt{5} = 2.236)$$

$$[\text{OH}^-] = 10^{-7} + 0.618 \times 10^{-7} = 1.618 \times 10^{-7}$$

$$\text{pOH} = 7 - \log(1.618) = 6.79$$

$$\text{pH} = 14 - 6.79 = 7.21$$

**Exercise**

1. Calculate pH of a KOH solution having

(a) 5.6 g of KOH mixed in 50 mL water

(b) if it is further diluted to make 100 mL

Ans. (a) 14.3 (b) 14

(c) **pH of mixture of two strong acids :** If  $V_1$  volume of a strong acid solution of normality  $N_1$  is mixed with  $V_2$  volume of another strong acid solution of normality  $N_2$ , then

$$\text{Number of } \text{H}^+ \text{ ions from I-solution} = N_1 V_1$$

$$\text{Number of } \text{H}^+ \text{ ions from II- solution} = N_2 V_2$$

If final normality is  $N$  and final volume of  $V$ , then

$$NV = N_1 V_1 + N_2 V_2$$

[Dissociation equilibrium of none of these acids will be disturbed as both are strong acid]

$$[\text{H}^+] = N = \frac{N_1 V_1 + N_2 V_2}{V_1 + V_2}$$

(d) **pH of mixture of two strong bases :** Similar to above calculation

$$[\text{OH}^-] = N = \frac{N_1 V_1 + N_2 V_2}{V_1 + V_2}$$

$$[\text{H}^+] = \frac{10^{-14}}{[\text{OH}^-]}$$

**Illustration**

1. 500 mL of  $10^{-5}$  M NaOH is mixed with 500 mL of  $2.5 \times 10^{-5}$  M of  $\text{Ba}(\text{OH})_2$ . To the resulting solution 99 L water is added. Calculate pH.

Sol.  $[\text{OH}^-] = \frac{500 \times 10^{-5} + 500 \times 2 \times 2.5 \times 10^{-5}}{1000}$  (Normality of  $\text{Ba}(\text{OH})_2 = 2 \times 2.5 \times 10^{-5}$ )

$$= 3 \times 10^{-5} \text{ M}$$

$$M_1 = 3 \times 10^{-5} \text{ M}$$

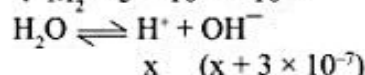
$$V_1 = 1 \text{ L}$$

$$V_2 = 100 \text{ L}$$

no. of moles of  $[\text{OH}^-]$  initially = no. of moles of  $[\text{OH}^-]$ , in final solution.

$$3 \times 10^{-5} = M_2 \times 100$$

$$\therefore M_2 = 3 \times 10^{-7} < 10^{-6}$$



$$K_w = x(x + 3 \times 10^{-7}) = 10^{-14}$$

$$\therefore x = \left( \frac{\sqrt{13} - 3}{2} \right) \times 10^{-7}$$

$$x = 0.302 \times 10^{-7}$$

$$[\text{OH}^-]_{\text{Net}} = \left[ 3 + \frac{\sqrt{13} - 3}{2} \right] \times 10^{-7} = \left[ \frac{3 + \sqrt{13}}{2} \right] \times 10^{-7} = 3.302 \times 10^{-7}$$

**Exercise**

1. Calculate the pH for-  
 (a) 50 mL of 0.1 M HCl, 25 mL of 0.1 M  $\text{H}_2\text{SO}_4$ , 25 mL of 0.2 M  $\text{HNO}_2$  + 100 mL of  $\text{H}_2\text{O}$   
 (b) 50 mL of 0.2 M NaOH + 100 mL of 0.1 M RbOH the resulting solution is diluted by 350 mL  $\text{H}_2\text{O}$ .

Ans. (a) 1.123 (b) 12.6

**(e) pH of mixture of a strong acid and a strong base :**

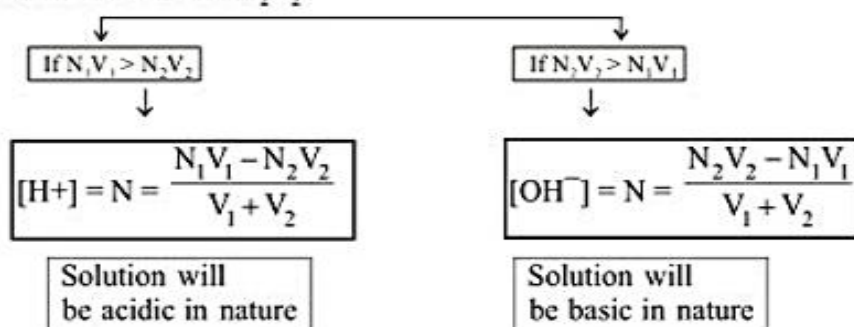
Acid base neutralisation reaction will take place.

The solution will be acidic or basic depending on which component is taken in excess.

If  $V_1$  volume of a strong acid solution of normality  $N_1$  is mixed with  $V_2$  volume of a strong base solution normality  $N_2$ , then

$$\text{Number of } \text{H}^+ \text{ ions from I-solution} = N_1 V_1$$

Number of  $\text{OH}^-$  ions from II-solution =  $N_2 V_2$



$$[\text{H}^+] = \frac{10^{-14}}{[\text{OH}^-]}$$

### Illustration

1. Calculate pH of mixture of  $(400 \text{ mL}, \frac{1}{200} \text{ M Ba(OH)}_2) + (400 \text{ mL}, \frac{1}{50} \text{ M HCl}) + (200 \text{ mL of water})$

Sol. 
$$[\text{H}^+] = \frac{400 \times \frac{1}{50} - 400 \times \frac{1}{200} \times 2}{1000} = 4 \times 10^{-3}, \text{ so pH} = 3 - 2 \log 2 = 2.4$$

2. What will be resultant pH when 150 mL of an aqueous solution of HCl (pH = 2.0) is mixed with 350 mL of an aqueous solution of NaOH (pH = 12.0)?

Sol. pH of HCl = 2

$$\therefore [\text{HCl}] = 10^{-2} \text{ M}$$

pH of NaOH = 12,

$$\text{pOH} = 2$$

$$\therefore [\text{NaOH}] = 10^{-2} \text{ M}$$

	HCl	+	NaOH	→	NaCl	+	H <sub>2</sub> O
Meq. initial	150 × 10 <sup>-2</sup>		350 × 10 <sup>-2</sup>		0		0
	= 1.5		= 3.5				
Meq. final	0		2		1.5		1.5

$$\therefore [\text{OH}^-] \text{ from NaOH} = \frac{2}{500} = 4 \times 10^{-3} \text{ M}$$

$$\text{pOH} = -\log [\text{OH}^-] = -\log (4 \times 10^{-3})$$

$$\therefore \text{pOH} = 2.3979$$

$$\therefore \text{pH} = 14 - \text{pOH} = 14 - 2.3979 = 11.6021$$

### Exercise

1. Calculate pH of mixture 200 mL of 0.2 M  $\text{H}_2\text{SO}_4$  + 300 mL of 0.2 M NaOH + 200 mL of 0.1 M KOH.

Ans. 7

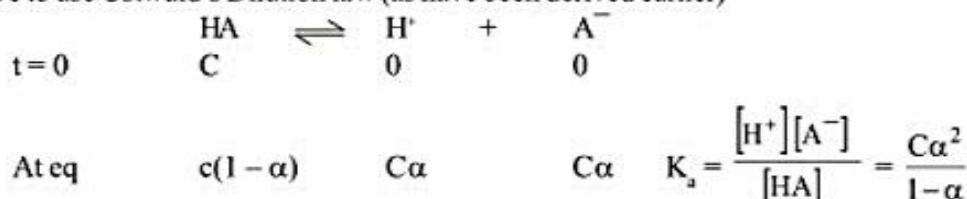
2. Calculate the pH when 200 mL of 0.25 M  $\text{H}_2\text{SO}_4$  is mixed with 200 mL of 0.2 M  $\text{Ba(OH)}_2$

Ans. 1.30

**(f) pH of a weak acid (monoprotic) solution :**

Weak acid does not dissociate 100% therefore we have to calculate the percentage dissociation using ( $K_a$ ) dissociation constant of the acid.

We have to use Ostwald's Dilution law (as have been derived earlier)



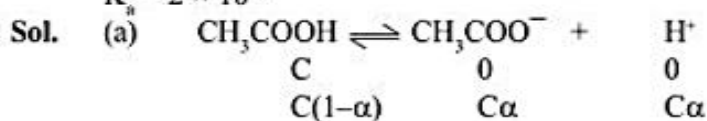
$$\text{If } \alpha \ll 1 \Rightarrow (1-\alpha) \approx 1 \Rightarrow K_a = C\alpha^2 \Rightarrow \alpha = \sqrt{\frac{K_a}{C}} \text{ (is valid if } \alpha < 0.5)$$

$$[\text{H}^+] = C\alpha = C \sqrt{\frac{K_a}{C}} = \sqrt{K_a \times C} \text{ So } \text{pH} = \frac{1}{2} (\text{p}K_a - \log C)$$

On increasing the dilution  $\Rightarrow C \downarrow = \alpha \uparrow$  and  $[\text{H}^+] \downarrow \Rightarrow \text{pH} \uparrow$

**Illustration**

1. Calculate pH of (a)  $10^{-1} \text{ M CH}_3\text{COOH}$  (b)  $10^{-3} \text{ M CH}_3\text{COOH}$   
 $K_a = 2 \times 10^{-5}$



$$K_a = \frac{C\alpha^2}{1-\alpha} \Rightarrow \alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{2 \times 10^{-5}}{10^{-1}}} = \sqrt{2 \times 10^{-4}} \quad (\alpha \ll 0.1)$$

$$\text{So, } [\text{H}^+] = 10^{-1} \times \sqrt{2} \times 10^{-2} \Rightarrow \text{pH} = 3 - \frac{1}{2} \log 2 = 2.85$$

$$(b) \quad \alpha = \sqrt{\frac{K_a}{C}} \Rightarrow \alpha = \sqrt{\frac{2 \times 10^{-5}}{10^{-3}}} = \sqrt{2 \times 10^{-2}} \quad (\alpha > 0.1)$$

Since  $\alpha > 0.1$ , exact calculation is required.

$$K_a = \frac{C\alpha^2}{1-\alpha} \Rightarrow 2 \times 10^{-5} = \frac{10^{-3} \times \alpha^2}{1-\alpha} \Rightarrow \alpha = 13.14\%$$

$$[\text{H}^+] = 10^{-3} \times 0.1314 = 1.314 \times 10^{-4} \Rightarrow \text{pH} = 4 - \log(1.314) \approx 3.8$$

**Exercise**

1. Calculate pH of (a)  $10^{-4} \text{ M CH}_3\text{COOH}$  (b)  $10^{-6} \text{ M CH}_3\text{COOH}$   
 Take  $K_a = 2 \times 10^{-5}$

Ans. (a) 4.04 (b) 6.022



**Note :** At very low concentration (at infinite dilution) weak electrolyte will be almost 100% dissociate, so behaves as strong electrolyte

(pH) of  $10^{-6}$  M HCl = pH of  $10^{-6}$  M  $\text{CH}_3\text{COOH}$  = 6)

**(g) pH of a mixture of weak acid (monoprotic) and a strong acid solution :**

Weak acid and strong acid both will contribute  $\text{H}^+$  ion.

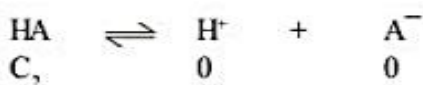
For the first approximation we can neglect the  $\text{H}^+$  ions coming from the weak acid solution and calculate the pH of the solution from the concentration of the strong acid only.

To calculate exact pH, we have to take the effect of presence of strong acid on the dissociation equilibrium of the weak acid.

If  $[\text{SA}] = C_1$  and  $[\text{WA}] = C_2$ , then  $[\text{H}^+]$  from  $\text{SA} = C_1$   
the weak acid will dissociate as follows,

(SA = Strong acid)

(WA = Weak acid)



$$\begin{array}{ccccc} C_2(1-\alpha) & & C_2\alpha + C_1 & & C_2\alpha \end{array} \quad K_a = \frac{(C_2\alpha + C_1)C_2\alpha}{C_2(1-\alpha)} \quad (\alpha \ll 1)$$

(The weak acids dissociation will be further suppressed because of presence of strong acid, common ion effect)

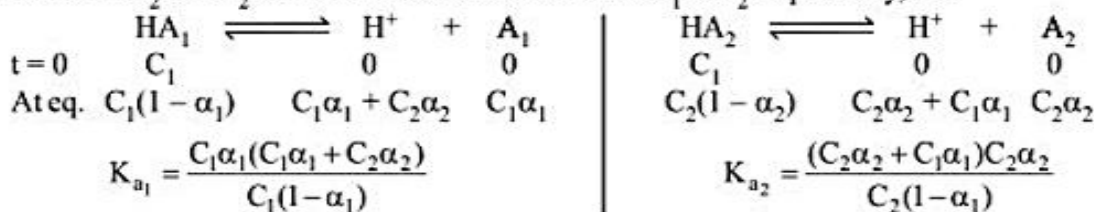
$$K_a = (C_2\alpha + C_1) \alpha$$

To  $\text{H}^+$  ion concentration =  $C_1 + C_2\alpha$

If the total  $[\text{H}^+]$  from the acid is more than  $10^{-6}$  M, then contribution from the water can be neglected, but if comparable then we take  $[\text{H}^+]$  from water also.

**(h) pH of a mixture of two weak acid (both monoprotic) solution :**

- Both acids will dissociate partially
- Let the acid are  $\text{HA}_1$  &  $\text{HA}_2$  and their final concentrations are  $C_1$  &  $C_2$  respectively, then



(Since  $\alpha_1, \alpha_2$  both are small in comparison to unity)

$$K_{a1} = (C_1\alpha_1 + C_2\alpha_2) \alpha_1 : K_{a2} = (C_1\alpha_1 + C_2\alpha_2) \alpha_2 \Rightarrow \frac{K_{a1}}{K_{a2}} = \frac{\alpha_1}{\alpha_2}$$

$$[\text{H}^+] = C_1\alpha_1 + C_2\alpha_2 = \frac{C_1K_{a1}}{\sqrt{C_1K_{a1} + C_2K_{a2}}} + \frac{C_2K_{a2}}{\sqrt{C_1K_{a1} + C_2K_{a2}}} \Rightarrow [\text{H}^+] = \sqrt{C_1K_{a1} + C_2K_{a2}}$$

- If the dissociation constant of one of the acid is very much greater than that of the second acid then contribution from the second acid can be neglected.

$$\text{So, } [\text{H}^+] = C_1\alpha_1 + C_2\alpha_2 = C_1\alpha_1$$

**Illustration**

1. Calculate pH of solution obtained by mixing equal vol. of 0.02 M HOCl & 0.2 M CH<sub>3</sub>COOH solution given that

$$K_{a_1} [\text{HOCl}] = 2 \times 10^{-4}$$

$$K_{a_2} [\text{CH}_3\text{COOH}] = 2 \times 10^{-5}$$

also calculate OH<sup>-</sup>, OCl<sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup>

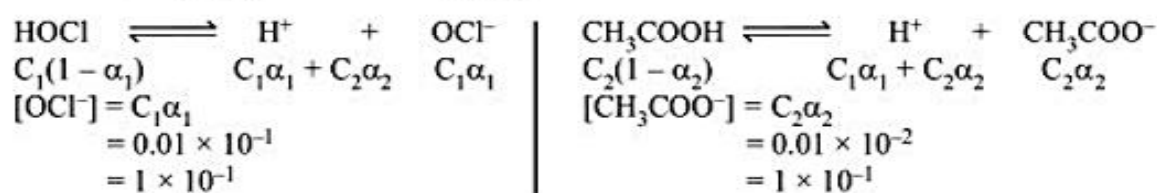
**Sol.** Final solution volume become double

$$C_1 = 0.01 \quad C_2 = 0.1$$

$$[\text{H}^+] = \sqrt{K_{a_1} C_1 + K_{a_2} C_2} = \sqrt{2 \times 10^{-4} \times 0.01 + 2 \times 10^{-5} \times 0.1} = \sqrt{2 \times 10^{-6} + 2 \times 10^{-6}} = 2 \times 10^{-3}$$

$$\text{pH} = 3 - \log 2 = 3 - 0.3010 = 2.69$$

$$\alpha_1 = \frac{2 \times 10^{-4}}{2 \times 10^{-3}} = 10^{-1} \quad \alpha_2 = \frac{2 \times 10^{-5}}{2 \times 10^{-3}} = 10^{-2}$$



$$[\text{OH}^-] = \frac{K_w}{[\text{H}^+]} = \frac{10^{-14}}{2 \times 10^{-3}} = 0.5 \times 10^{-11}$$

$$= 5 \times 10^{-12} \text{ M}$$

$$[\text{HOCl}] = 10^{-2} (1 - 0.01) = 9 \times 10^{-3} \text{ M}$$

$$[\text{CH}_3\text{COOH}] = 10^{-1} (1 - 0.01) \approx 10^{-1}$$

**Exercise**

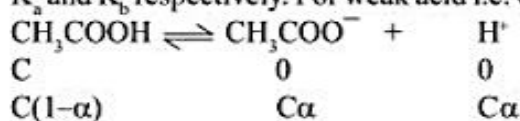
1. Calculate pH of solution obtained by mixing equal vol. of 2 M HOCl & 3 M HA solution given that

$$K_{a_1} [\text{HOCl}] = 2 \times 10^{-4}, \quad K_{a_2} [\text{HA}] = 2 \times 10^{-5}$$

**Ans.** 1.4

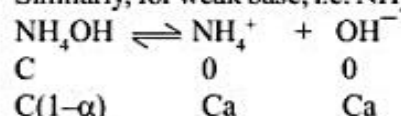
**RELATIVE STRENGTH OF WEAK ACIDS AND BASES**

The relative strength of weak acids and bases are generally determined by their dissociation constants  $K_a$  and  $K_b$  respectively. For weak acid i.e. CH<sub>3</sub>COOH



$$K_a = \frac{C\alpha \cdot C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)} \Rightarrow K_a = C\alpha^2 \quad (\text{if } \alpha \ll 1)$$

Similarly, for weak base, i.e.  $\text{NH}_4\text{OH}$



$$K_b = C\alpha^2$$

$K_a$  and  $K_b$  are just the equilibrium constants and hence depends only on temperature. Greater the value of dissociation constant of the acid ( $K_a$ ), more is the strength of the acid and greater the value of dissociation constant of the base, more is the strength of the base. For two acids of equimolar concentration.

$$\frac{\text{Strength of acid (I)}}{\text{Strength of acid (II)}} = \sqrt{\frac{K_{a_1}}{K_{a_2}}}$$

$$\text{Similarly for bases, } \frac{\text{Strength of base (I)}}{\text{Strength of base (II)}} = \sqrt{\frac{K_{b_1}}{K_{b_2}}}$$

The modern method is to convert  $K_a$  as a power of 10 and express acid strength by power of 10 with sign changed and call this new unit  $\text{p}K_a$ . Thus, if  $K_a$  for acid is equal to  $10^{-4}$ ,  $\text{p}K_a = 4$ . So higher  $\text{p}K_a$  value means lower acid strength,

that is  $\text{p}K_a = -\log K_a$

Also,  $\text{p}K_b = -\log K_b$

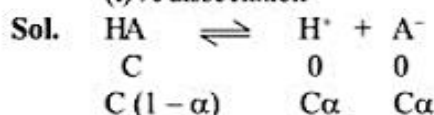
### Illustration

1.  $K_a$  for acid HA is  $2.5 \times 10^{-8}$  calculate for its decimolar solution at  $25^\circ\text{C}$ .

(i) % dissociation

(ii) pH

(iii)  $\text{OH}^-$  ion concentration



$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \Rightarrow \frac{C\alpha \cdot C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)} = C\alpha^2$$

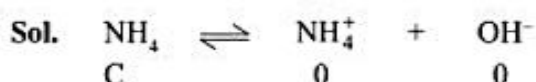
$$\begin{aligned} \text{(i)} \quad \therefore \quad \alpha &= \sqrt{\frac{K_a}{C}} = \sqrt{\frac{2.5 \times 10^{-8}}{1/10}} \quad (C = 1/10 \text{ M}) \\ &= 5 \times 10^{-4} = 0.05\% \end{aligned}$$

$$\text{(ii)} \quad [\text{H}^+] = C\alpha = \frac{1}{10} \times 5 \times 10^{-4} \text{ mol/L} \Rightarrow \text{So pH} = 5 - \log 5 = 4.30$$

$$\text{(iii)} \quad [\text{H}^+][\text{OH}^-] = 1 \times 10^{-14}$$

$$\therefore [\text{OH}^-] = \frac{10^{-14}}{5 \times 10^{-4}} = 2 \times 10^{-10} \text{ mol/L}$$

2. Determine the degree of dissociation of 0.05 M  $\text{NH}_3$  at  $25^\circ\text{C}$  in a solution of  $\text{pH} = 10$ .



Given,  $\text{pH} = 10$

$$[\text{H}^+] = 10^{-10}$$

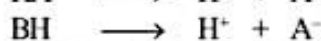
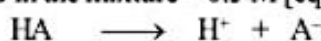
$$[\text{H}^+][\text{OH}^-] = 1 \times 10^{-14}$$

$$\therefore [\text{OH}^-] = \frac{1 \times 10^{-14}}{10^{-10}} = 10^{-4} = C\alpha$$

$$\therefore \alpha = \frac{[\text{OH}^-]}{C} = \frac{10^{-4}}{0.05} = 2 \times 10^{-3} \text{ or } 0.2\%$$

3. Two weak monobasic organic acids HA and HB have dissociation constants as  $1.6 \times 10^{-5}$  and  $0.4 \times 10^{-5}$  respectively at  $25^\circ\text{C}$ . If 500 mL of 1 M solutions of each of these two acids are mixed to produce 1 litre of solution, what is the  $\text{pH}$  of the resulting solution?

Sol. In such cases, we have to consider  $\text{H}^+$  from both HA and HB simultaneously. The concentration of HA and HB in the mixture = 0.5 M [equal volumes are mixed] = say 'c'



Let,  $x = [\text{H}^+]$  from HA and  $y = [\text{H}^+]$  from HB

$$\Rightarrow [\text{H}^+]_{\text{final}} = x + y$$

$$K_{\text{HA}} = \frac{(x+y)x}{C} \quad \text{and} \quad K_{\text{HB}} = \frac{(x+y)y}{C}$$

$$\frac{[\text{H}^+]_{\text{HA}}}{[\text{H}^+]_{\text{HB}}} = \frac{x}{y} = \sqrt{\frac{K_{\text{HA}} \times C}{K_{\text{HB}} \times C}}$$

$$\frac{x}{y} = \sqrt{\frac{1.6 \times 10^{-5}}{0.4 \times 10^{-5}}} = 2$$

$$x = 2y \Rightarrow y = \frac{x}{2}$$

$$\text{Substitute for } y = \frac{x}{2} \text{ in } K_{\text{HA}} = \frac{x^2 + xy}{c}$$

$$1.6 \times 10^{-5} = \frac{2x^2 + x^2}{2 \times 0.5}$$

$$3x^2 = 1.6 \times 10^{-5} \Rightarrow x^2 = 5.33 \times 10^{-6}$$

$$x = 2.30 \times 10^{-3} \text{ M}, \quad y = 1.15 \times 10^{-3} \text{ M}$$

$$[\text{H}^+]_{\text{Final}} = x + y = 2.30 \times 10^{-3} + 1.15 \times 10^{-3} = 3.45 \times 10^{-3} \text{ M}$$

$$\text{pH} = -\log_{10}(3.45 \times 10^{-3})$$

$$\text{pH} = 2.462$$



### Exercise

1. Saccharin ( $K_a = 2 \times 10^{-12}$ ) is a weak acid represented by formula  $\text{HSaC}$ . A  $8 \times 10^{-4}$  mole amount of Saccharin is dissolved in  $400 \text{ cm}^3$  water of  $\text{pH} = 3$ . Assuming no change in volume, calculate the concentration of  $\text{SaC}^-$  ions in the resulting solution at equilibrium.

Ans.  $[\text{SaC}^-] = 4 \times 10^{-12} \text{ M}$

2. A solution contains  $0.08 \text{ M HCl}$ ,  $0.08 \text{ M CHCl}_2\text{COOH}$  and  $0.1 \text{ CH}_3\text{COOH}$ . The  $\text{pH}$  of this solution is 1. If  $K_a$  for acetic acid is  $10^{-5}$ , calculate  $K_a$  for  $\text{CHCl}_2\text{COOH}$ .

Ans.  $K_a = 3.33 \times 10^{-2}$

### ISOHYDRIC SOLUTIONS

- (i) Solution of electrolytes are said to be isohydric if the concentration of the common ion present in them is the same and on mixing such solution, there occurs no change in the degree of dissociation of either of the electrolyte.
- (ii) Let the isohydric solution is made by  $\text{HA}_1$  and  $\text{HA}_2$  acids, then  $[\text{H}^+]$  of both should be equal i.e.

$$\sqrt{K_{a1} C_1} = \sqrt{K_{a2} C_2} \quad \text{or} \quad \frac{K_{a1}}{K_{a2}} = \frac{C_2}{C_1}$$

### Illustration

1. The degree of dissociation of pure water at  $25^\circ\text{C}$  is found to be  $1.8 \times 10^{-9}$ . Find  $K_w$  and  $K_d$  at  $25^\circ\text{C}$ .  
 (A)  $3.24 \times 10^{-18}$ ;  $5.83 \times 10^{-20}$  (B)  $1 \times 10^{-14}$ ;  $1.8 \times 10^{-15}$   
 (C)  $1.8 \times 10^{-16}$ ;  $1 \times 10^{-14}$  (D)  $1 \times 10^{-14}$ ;  $1 \times 10^{-14}$

Ans. (B)

Sol. Since  $\alpha = 1.8 \times 10^{-9}$

$$\text{and for water } C = \frac{1000}{18} = 55.56$$

$$[\text{H}^+] = [\text{OH}^-] = C\alpha = 55.56 \times 1.8 \times 10^{-9} = 1 \times 10^{-7} \text{ M}$$

$$K_w = [\text{H}^+] \times [\text{OH}^-] = (1 \times 10^{-7})^2 = 10^{-14}$$

$$\text{and } K_d = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]} = \frac{K_w}{[\text{H}_2\text{O}]} = \frac{10^{-14}}{55.56} = 1.8 \times 10^{-16}$$

2. When a  $0.1 \text{ N}$  solution of an acid at  $25^\circ\text{C}$  has a degree of ionisation of  $4\%$ , the concentration of  $\text{OH}^-$  present is-  
 (A)  $2.5 \times 10^{-3}$  (B)  $2.5 \times 10^{-11}$  (C)  $2.5 \times 10^{-12}$  (D)  $2.5 \times 10^{-13}$

Ans. (C)

Sol.  $[\text{H}^+] = C\alpha = 0.1 \times 4 \times 10^{-2} = 4 \times 10^{-3} \text{ M}$  or  $[\text{OH}^-] = \frac{10^{-14}}{[\text{H}^+]} = 2.5 \times 10^{-12} \text{ N}$

### Exercise

1. Calculate the molar concentration of a solution of acetic (HOAc) that has a pH of 4.00.  
( $K_a = 1.8 \times 10^{-5}$ )

(A)  $1.0 \times 10^{-3}$  (B)  $1.0 \times 10^{-6}$  (C)  $0.057 \times 10^{-2}$  (D) 0.010

Ans. (C)

2. Select the correct option from the following ?

(A)  $pK_w$  increases with increase of temperature

(B)  $pK_w$  decreases with increase of temperature

(C)  $pK_w = 14$  at all temperature

(D)  $pK_w = pH$  at all temperature

Ans. (B)

### SALTS

(i) Salts are the ionic compounds formed when its positive part (Cation) come from a base and its negative part (Anion) come from an acid.

(ii) Salts may taste salty, bitter, astringer or sweet or tasteless

(iii) Solution of salts may be acidic, basic or neutral.

(iv) Fused salts and their aqueous solutions conduct electricity and undergo electrolysis

(v) The salts are generally crystalline solids

#### 1. Classification of salts :

These salts may be classified into four categories.

##### 1.1 Simple salts :

The salts formed by the neutralisation process between acid and base. These are of three types.

##### (i) Normal salt :

The salt formed by the loss of all possible protons (replaceable  $H^+$  ions)

Ex. NaCl,  $NaNO_3$ ,  $K_2SO_4$ ,  $Ca_3(PO_4)_2$ ,  $Na_3BO_3$ ,  $Na_2HPO_4$ ,  $NaH_2PO_4$  etc.

##### (ii) Acids salts :

Salts formed by incomplete neutralisation of polybasic acid. Such salts contain one or more replaceable H atom.

Ex.  $NaHCO_3$ ,  $NaHSO_4$ ,  $NaH_2PO_4$ ,  $Na_2HPO_4$  etc.

Above salts when neutralized by base form normal salts.

##### (iii) Basic salts :

Salts formed by incomplete neutralisation of poly acidic bases are called basic salts. These salt contain one or more hydroxyl groups.

Ex.  $Zn(OH)Cl$ ,  $Mg(OH)Cl$ ,  $Fe(OH)_2$ ,  $Bi(OH)_3$  etc.

Above salt when neutralised by acids form normal salts.

##### 1.2 Double salts :

(i) The addition compounds formed by the combination of two simple salts are termed as double salts.

**Ex.**  $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$  (Ferrous ammonium sulphate),  $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$  (Alum) and other alums.

(ii) Above salts are stable in solid state only.

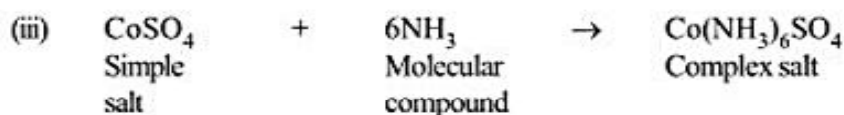
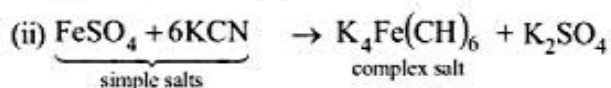
(iii) When dissolved in water, it furnishes all the ions present in the simple salt form which it has been constituted.

(iv) The solution of double salt shows the properties of the samples salts from which it has been constituted

### 1.3 Complex salts :

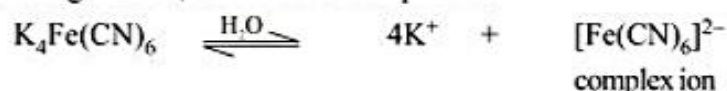
(i) They are formed by combination of simple salt or molecular compounds.

**Ex.**  $\text{K}_4\text{Fe}(\text{CN})_6$ ,  $\text{Co}(\text{NH}_3)_6\text{SO}_4$  etc.



(iv) These are stable in solid states as well as solutions

(v) On dissolving in water, it furnishes a complex ion.

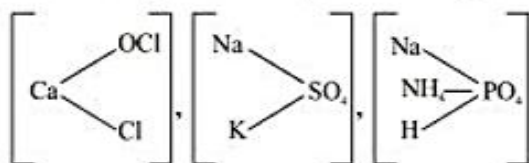


(vi) The properties of the solution are different from the properties of the substance from which it has been constituted.

### 1.4 Mixed salts :

(i) The salt which furnishes more than one cation or more than one anion when dissolved in water is called mixed salt.

**Ex.**  $\text{CaOCl}_2$ ,  $\text{NaKSO}_4$ ,  $\text{NaNH}_4\text{HPO}_4$  etc.



## HYDROLYSIS OF SALTS

Salts are the product of an acid and a base, other than water. Depending on the nature of an acid or a base there can be four types of salts:

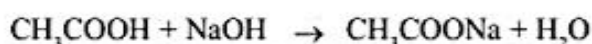
- (i) Salt of a weak acid and a strong base.
- (ii) Salt of a strong acid and a weak base.
- (iii) Salt of a weak acid and a weak base and
- (iv) Salt of a strong acid and a strong base.

We shall first look at what is hydrolysis and then find out how to calculate the pH due to it.

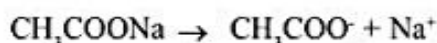


### 1. Salt of a Weak Acid and Strong Base

Let us take a certain amount of weak acid ( $\text{CH}_3\text{COOH}$ ) and add to it the same amount (equivalents) of a strong base ( $\text{NaOH}$ ). They will react to produce  $\text{CH}_3\text{COONa}$ .



$\text{CH}_3\text{COONa}$  being a strong electrolyte, completely dissociates into its constituent ions.



Now, the ions produced would react with  $\text{H}_2\text{O}$ . This process is called hydrolysis.



We know that  $\text{NaOH}$  is a strong base and therefore it would be completely dissociated to give  $\text{Na}^+$  and  $\text{OH}^-$  ions.



Cancelling  $\text{Na}^+$  on both the sides,



*We can note here that ions coming from strong bases do not get hydrolysed. We should note here that the solution will be basic. This is because the amount of  $\text{CH}_3\text{COOH}$  produced and  $\text{OH}^-$  produced are equal. But  $\text{CH}_3\text{COOH}$  will not completely dissociate to give  $\text{H}^+$  ions. Therefore  $[\text{OH}^-]$  ions will be greater than  $[\text{H}^+]$  ions.*

Since the reaction is at equilibrium,

$$K_c = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]}$$

This equilibrium constant  $K_c$  is given a new symbol,  $K_b$ .

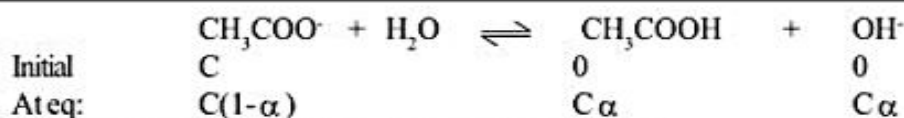
$$\therefore K_b = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]}$$

If we multiply and divide the above equation by  $[\text{H}^+]$  of the solution, then

$$K_b = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-][\text{H}^+]}{[\text{CH}_3\text{COO}^-][\text{H}^+]} = \frac{[\text{H}^+][\text{OH}^-]}{\frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]}}$$

$$K_b = \frac{K_w}{K_a} \Rightarrow K_b = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} = \frac{K_w}{K_a}$$





Where  $\alpha$  is the degree of hydrolysis of  $\text{CH}_3\text{COO}^-$  ion?

$$\therefore \frac{C\alpha \times C\alpha}{C(1-\alpha)} = \frac{K_w}{K_a}$$

If  $\alpha$  is very much less than 1,

$$C\alpha^2 = \frac{K_w}{K_a}, \quad \alpha = \sqrt{\frac{K_w}{K_a C}}$$

$$\text{As } [\text{OH}^-] = C\alpha, \quad [\text{OH}^-] = C \times \sqrt{\frac{K_w}{K_a C}} = \sqrt{\frac{K_w C}{K_a}}$$

$$[\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \sqrt{\frac{K_w K_a}{C}} \quad \text{or} \quad \text{pH} = -\log[\text{H}^+] = -\log\left(\sqrt{\frac{K_w K_a}{C}}\right) = \frac{1}{2}\text{p}K_w + \frac{1}{2}\text{p}K_a + \frac{1}{2}\log C$$

### Illustration

1. Find out pH,  $h$  and  $[\text{OH}^-]$  of milli molar solution of KCN if the dissociation constant of HCN is  $10^{-7}$ .

**Sol.** (1)  $\text{pH} = 7 + 1/2 \text{p}K_a + 1/2 \log C = 7 + 1/2 \times 7 + 1/2 \log 10^{-3}$

$$= 7 + 7/2 - 3/2 \log 10 = \frac{14 + 7 - 3}{2} = \frac{21 - 3}{2} = 9$$

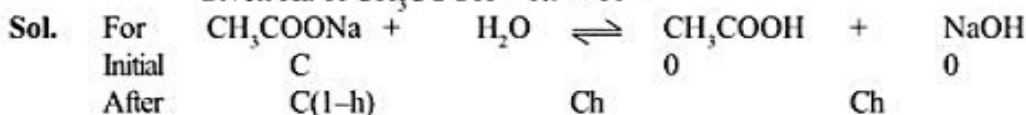
$$(2) \quad h = \sqrt{\frac{K_h}{C}} = \sqrt{\frac{10^{-14} \times 10^{-3}}{10^{-7}}} = 10^{-5}$$

$$(3) \quad [\text{OH}^-] = \sqrt{\frac{K_w \times C}{K_a}} = \sqrt{\frac{10^{-14} \times 10^{-3}}{10^{-7}}} = 10^{-5}$$

2. Calculate for 0.01 N solution of sodium acetate

(i) Hydrolysis constant (ii) Degree of hydrolysis (iii) pH

Given  $K_a$  of  $\text{CH}_3\text{COOH} = 1.9 \times 10^{-5}$



$$(i) \quad K_h = \frac{K_w}{K_a} = \frac{10^{-14}}{1.9 \times 10^{-5}} = 5.26 \times 10^{-10}$$

$$(ii) \quad h = \sqrt{\frac{K_h}{C}} = \sqrt{\frac{5.26 \times 10^{-10}}{0.01}} = 2.29 \times 10^{-6} \text{ M}$$

$$(iii) \quad [\text{OH}^-] \text{ from NaOH, a strong base} = Ch = 0.01 \times 2.29 \times 10^{-4} = 2.29 \times 10^{-6} \text{ M}$$

$$\text{pOH} = 5.64$$

$$\therefore \text{pH} = 14 - 5.64 = 8.36$$

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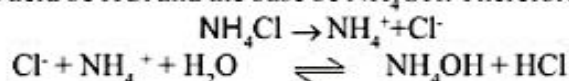
**Exercise**


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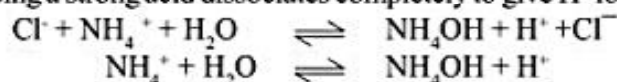
1. Calculate the pH and degree of hydrolysis of 0.01 M solution of NaCN,  $K_a$  for HCN is  $6.2 \times 10^{-12}$ .  
**Ans.** pH = 11.6  
Degree of hydrolysis =  $4 \times 10^{-11}$
  2. Calculate the pH after the addition of 90 ml and 100 ml respectively of 0.1 N NaOH to 100 ml 0.1 N  $\text{CH}_3\text{COOH}$  (Given  $pK_a$  for  $\text{CH}_3\text{COOH}$  = 4.74)  
**Ans.** pH = 8.71
- 

**2. Salt of a Weak Base and a Strong Acid**

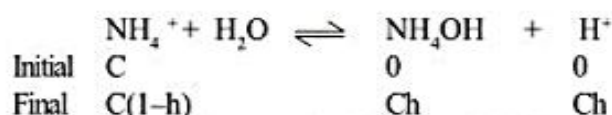
Let the acid be HCl and the base be  $\text{NH}_4\text{OH}$ . Therefore the salt would be  $\text{NH}_4\text{Cl}$ .



HCl being a strong acid dissociates completely to give  $\text{H}^+$  ions and  $\text{Cl}^-$  ions.



We can see that the ion coming from the strong acid does not get hydrolysed. We had previously seen that the ion coming from the strong base also does not get hydrolyzed. Hence, one can conclude that the salt of a strong acid and strong base does not get hydrolyzed. In this hydrolysis,  $\text{NH}_4\text{OH}$  and  $\text{H}^+$  are being produced. This implies that the solution is acidic. To calculate pH,



Where  $h$  is the degree of hydrolysis of  $\text{NH}_4^+$ .

$$K_b = \frac{[\text{NH}_4\text{OH}][\text{H}^+]}{[\text{NH}_4^+]}$$

Multiplying and dividing by  $\text{OH}^-$  and rearranging.

$$K_b = \frac{[\text{NH}_4\text{OH}][\text{H}^+][\text{OH}^-]}{[\text{NH}_4^+][\text{OH}^-]} \Rightarrow \frac{[\text{H}^+][\text{OH}^-]}{\frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]}} \Rightarrow \frac{K_w}{K_b} \therefore K_b = \frac{K_w}{K_b}$$

Now, substituting the concentrations,

$$K_b = \frac{[\text{NH}_4\text{OH}][\text{H}^+]}{[\text{NH}_4^+]} = \frac{K_w}{K_b} = \frac{Ch \times Ch}{C(1-h)} = \frac{Ch^2}{1-h}$$

$$\text{If } h \leq 0.1, \text{ then } Ch^2 = \frac{K_w}{K_b} \Rightarrow h = \sqrt{\frac{K_w}{K_b C}}$$

Since  $[\text{H}^+] = Ch$ ,  $[\text{H}^+] = C \sqrt{\frac{K_w}{K_b C}} = \sqrt{\frac{K_w C}{K_b}}$  or  $\text{pH} = \frac{1}{2} \text{p}K_w - \frac{1}{2} \text{p}K_b - \frac{1}{2} \log C$

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**Illustration**

1. Find out the  $K_h$  of centi normal [ $10^{-2}$  N] solution of  $\text{NH}_4\text{Cl}$  (SA-WB) if dissociation constant of  $\text{NH}_4\text{OH}$  is  $10^{-6}$  and  $K_w = 10^{-14}$ . Find out degree of hydrolysis and also find  $[\text{H}^+]$  and pH of solution?

Given :  $K_w = 10^{-14}$ ;  $K_b = 10^{-6}$

**Sol.** (1)  $K_h = \frac{K_w}{K_b} = \frac{10^{-14}}{10^{-6}} = 10^{-8}$

(2)  $h = \sqrt{\frac{K_h}{C}} = \sqrt{\frac{10^{-8}}{10^{-2}}} = \sqrt{10^{-6}} = 10^{-3}$

(3)  $[\text{H}^+] = Ch$   
 $= 10^{-2} \times 10^{-3}$   
 $= 10^{-5}$

(4)  $\text{pH} = -\log [\text{H}^+] = -\log [10^{-5}]$   
 $= +\log [10^{-5}] = +5 \times 1 = 5$

2. How many grams of  $\text{NH}_4\text{Cl}$  should be dissolved per litre of solution to have a pH of 5.13 ?  $K_b$  for  $\text{NH}_3$  is  $1.8 \times 10^{-5}$ .

**Sol.**  $\text{NH}_4\text{Cl}$  is a salt of strong acid and weak base for solutions of such salts.

$$\text{pH} = \frac{1}{2} [\text{p}K_w - \log C - \text{p}K_b]$$

$$\Rightarrow 10.26 = 14 - \log C - 4.74$$

$$\Rightarrow \log C = 9.26 - 10.26 = -1.0$$

$$\therefore C = 10^{-1} \text{ M}$$

$$[\text{NH}_4\text{Cl}] = 10^{-1} \text{ M}$$

$$W_{\text{NH}_4\text{Cl}} = 10^{-1} \times 53.5 \text{ gL}^{-1} = 5.35 \text{ gL}^{-1}$$

**Exercise**

1. Find out the  $K_h$  at 363 K ( $90^\circ\text{C}$ ) of a salt of [Strong acid - Weak base] if the value of  $K_b$  is  $10^{-5}$  [At  $90^\circ\text{C}$   $K_w = 10^{-12}$ ]

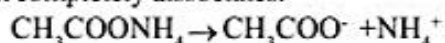
**Ans.**  $K_h = \frac{K_w}{K_b} = \frac{10^{-12}}{10^{-5}} = 10^{-7}$

2. What is the pH of 0.4 M aqueous  $\text{NaCN}$  solution ? {Given  $\text{p}K_b$  of  $\text{CN}^- = 4.70$ }

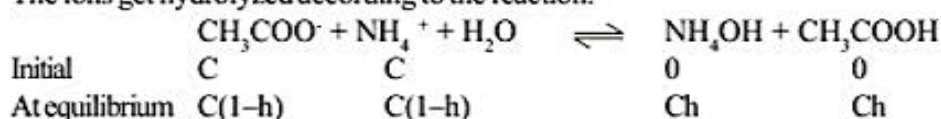
**Ans.**  $\text{pH} = 11.45$

**3. Salt of a Weak Acid and Weak Base**

Let the weak acid be  $\text{CH}_3\text{COOH}$  and the weak base be  $\text{NH}_4\text{OH}$ . Therefore, the salt is  $\text{CH}_3\text{COONH}_4$ . The salt completely dissociates.



The ions get hydrolyzed according to the reaction.



$$K_h = \frac{[\text{NH}_4\text{OH}][\text{CH}_3\text{COOH}]}{[\text{NH}_4^+][\text{CH}_3\text{COO}^-]}$$

Multiplying and dividing by  $\text{H}^+$  &  $\text{OH}^-$  and rearranging.

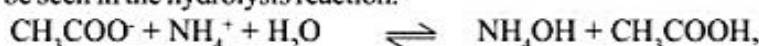
$$K_h = \frac{[\text{NH}_4\text{OH}][\text{CH}_3\text{COOH}][\text{H}^+][\text{OH}^-]}{[\text{NH}_4^+][\text{CH}_3\text{COO}^-][\text{H}^+][\text{OH}^-]} \Rightarrow \frac{[\text{H}^+][\text{OH}^-]}{\frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} \times \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]}} \Rightarrow \frac{K_w}{K_a K_b}$$

$$\therefore K_h = \frac{K_w}{K_a K_b}$$

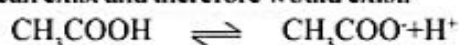
Substituting the concentration terms,

$$K_h = \frac{K_w}{K_a K_b} \quad \frac{Ch}{C(1-h)} \cdot \frac{Ch}{C(1-h)} \quad \frac{(Ch)^2}{[C(1-h)]^2} = \frac{h^2}{(1-h)^2}$$

As can be seen in the hydrolysis reaction.

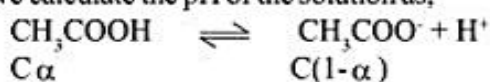


$\text{CH}_3\text{COOH}$  is present in the solution. This implies that the equilibrium between  $\text{CH}_3\text{COOH}$ ,  $\text{CH}_3\text{COO}^-$  and  $\text{H}^+$  can exist and therefore would exist.



In fact the equilibrium between  $\text{NH}_4\text{OH}$ ,  $\text{NH}_4^+$  and  $\text{OH}^-$  also exists.

Now, we calculate the pH of the solution as,



$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} = \frac{C(1-\alpha)(\text{H}^+)}{C\alpha} \quad \therefore [\text{H}^+] = K_a \times \left( \frac{\alpha}{1-\alpha} \right)$$

$$\text{Substituting } \frac{\alpha}{1-\alpha} \text{ as } \sqrt{\frac{K_w}{K_a K_b}}$$

$$[\text{H}^+] = K_a \times \left( \frac{\alpha}{1-\alpha} \right) = K_a \times \sqrt{\frac{K_w}{K_a K_b}} = \sqrt{\frac{K_w K_a}{K_b}}$$

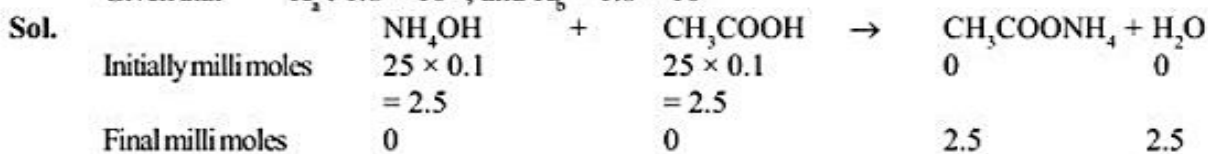
$$\text{or } \text{pH} = \frac{1}{2} \text{p}K_w + \frac{1}{2} \text{p}K_a - \frac{1}{2} \text{p}K_b$$



**Illustration**

1. Calculate pH of the mixture (25 mL of 0.1 M  $\text{NH}_4\text{OH}$  + 25 mL of 0.1 M  $\text{CH}_3\text{COOH}$ )

Given that  $K_a : 1.8 \times 10^{-5}$ , and  $K_b = 1.8 \times 10^{-5}$



As salt is formed (salt of weak acid and weak base) and pH will be decided by salt hydrolysis

$$\text{pH} = \frac{\text{p}K_w + \text{p}K_a - \text{p}K_b}{2} = \frac{1}{2} (-\log 10^{-14} - \log 1.8 \times 10^{-5} + \log 1.8 \times 10^{-5}) = 7$$

2. In the following which one has highest/maximum degree of hydrolysis.

(A) 0.01 M  $\text{NH}_4\text{Cl}$  (B) 0.1 M  $\text{NH}_4\text{Cl}$   
 (C) 0.001 M  $\text{NH}_4\text{Cl}$  (D) Same

**Ans.** C

**Sol.**  $\left( h \sqrt{\frac{K_h}{C}} \text{ if } C \text{ decreases, } h \text{ increases} \right)$

**Exercise**

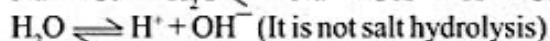
1. In the following which one has lowest value of degree of hydrolysis

(A) 0.01 M  $\text{CH}_3\text{COONH}_4$  (B) 0.1 M  $\text{CH}_3\text{COONH}_4$   
 (C) 0.001 M  $\text{CH}_3\text{COONH}_4$  (D) Same

**Ans.** D

**4. Salt of strong acid and strong base**

**Ex.**  $\text{NaCl}$ ,  $\text{BaCl}_2$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{KClO}_4$  etc.



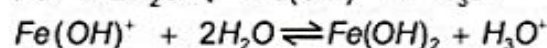
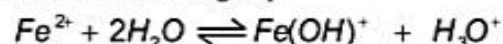
(a) No hydrolysis

(b) Solution is always neutral

(c)  $\text{pH} = 7$  at  $25^\circ\text{C}$

**5. Salt of a weak polyprotic acid and strong base**

- (i) **Salt containing multivalent cation or anion.** Hydrolysis of multivalent cation or anion takes place in stepwise manner and more than one hydrolytic products are formed. For example the hydrolysis of  $\text{Fe}^{2+}$  ions will occur in following steps



The hydrolysis constants  $K_{h_1}$  and  $K_{h_2}$  are

$$K_{h_1} = \frac{[\text{Fe}(\text{OH})^+][\text{H}_3\text{O}^+]}{[\text{Fe}^{2+}]} = \frac{K_w}{K_{b_2}}$$

$$K_{h_2} = \frac{[\text{Fe}(\text{OH})_2][\text{H}_3\text{O}^+]}{[\text{Fe}(\text{OH})^+]} = \frac{K_w}{K_{b_1}}$$

Where  $K_{b_1}$  and  $K_{b_2}$  are dissociation constants of  $\text{Fe}(\text{OH})_2$ . Since  $K_{b_1} \gg \gg K_{b_2}$  thus  $K_{h_1} \gg \gg K_{h_2}$  hence the hydrolysis of  $\text{Fe}(\text{OH})^+$  in comparison can be neglected and

$$[\text{H}_3\text{O}^+] = \sqrt{K_{h_1} C}$$

or 
$$\text{pH} = 7 - \frac{1}{2} \text{p}K_{b_2} - \frac{1}{2} \log C$$

- (ii) **Salt containing weak conjugate cation and an amphiprotic cation :** When a salt like  $\text{NaHCO}_3$ ,  $\text{NaHS}$ ,  $\text{NaH}_2\text{PO}_4$ ,  $\text{Na}_2\text{HPO}_4$  etc is dissolved in water the amphiprotic anion can either accept a proton from water (Hydrolysis) or can donate a proton to water. The pH of the solution can be calculated as

$$\text{pH} = \frac{1}{2} (\text{p}K_1 + \text{p}K_{a_2})$$

- (iii) **Salt containing strong conjugate cation and an amphiprotic cation :** Examples of such salts are  $\text{NH}_4\text{HCO}_3$ ,  $\text{NH}_4\text{HS}$  etc. The  $[\text{H}_3\text{O}^+]$  of the solution can be calculated as

$$[\text{H}_3\text{O}^+] = \sqrt{\frac{K_{a_1} K_w}{K_b} - K_{a_1} K_{a_2}}$$

- (iv) **Hydrolysis of amphiprotic anion**

Let us consider hydrolysis of amphiprotic anion only, i.e., when counter cation is not hydrolysed, example of some salts of this category are  $\text{NaHCO}_3$ ,  $\text{NaHS}$ ,  $\text{Na}_2\text{HPO}_4$ ,  $\text{NaH}_2\text{PO}_4$ .

Here,  $\text{H}_2\text{PO}_4^-$  and  $\text{HPO}_4^{2-}$  are amphiprotic anions. pH after their hydrolysis can be calculated as,

$$\text{pH of } \text{H}_2\text{PO}_4^- \text{ in aqueous medium} = (\text{p}K_{a_1} + \text{p}K_{a_2}) / 2$$

$$\text{pH of } \text{H}_2\text{PO}_2^- \text{ in aqueous medium} = (\text{p}K_{a_2} + \text{p}K_{a_3}) / 2$$

Here,  $\text{H}_2\text{PO}_4^{2-}$  is conjugate base of  $\text{H}_2\text{PO}_4^-$  and  $\text{H}_3\text{PO}_4$  is conjugate acid of  $\text{H}_2\text{PO}_4^-$ . Similarly,  $\text{PO}_4^{3-}$  is conjugate base of  $\text{HPO}_4^{2-}$  and  $\text{HPO}_4^{2-}$  is conjugate acid of  $\text{PO}_4^{3-}$ .

When these salts are dissolved in water,  $[\text{H}_3\text{O}^+]$  concentration can be determined as,

$$[\text{H}_3\text{O}^+] = \sqrt{K_{a_1} (K_w / k_b + K_{a_2})}$$

$$\text{pH} = -\log \sqrt{K_{a_1} (K_w / k_b + K_{a_2})}$$

### Hydrolysis at a Glance

	Salt	Nature	Degree	Hydrolysis Constant	pH
1.	NaCl (Strong acid + Strong Base)	Neutral	No Hydrolysis		
2.	CH <sub>3</sub> COONa (Weak acid + Strong base)	Basic	$h = \sqrt{k_w/Ck_a}$	$K_h = k_w/k_a$	$pH = 1/2[pk_w + pk_a + \log C]$
3.	NH <sub>4</sub> Cl (Strong acid + Weak base)	Acidic	$h = \sqrt{k_w/Ck_b}$	$K_h = k_w/k_b$	$pH = 1/2[pk_w - pk_b - \log C]$
4.	CH <sub>3</sub> COONH <sub>4</sub> (Weak acid + Weak base)	*	$h = \sqrt{k_w/(k_a + k_b)}$	$K_h = k_w/(k_a + k_b)$	$pH = 1/2[pk_w + pk_a - pk_b]$

In the case of salt of weak acid and weak base, nature of medium after hydrolysis is decided in the following manner:

- (i) If  $K_a = K_b$ , the medium will be neutral.
- (ii) If  $K_a > K_b$ , the medium will be acidic.
- (iii) If  $K_a < K_b$ , the medium will be basic.

The degree of hydrolysis of salts of weak acids and weak bases is unaffected by dilution because there is no concentration term in the expression of degree of hydrolysis.

**Note :** Degree of hydrolysis always increases with increase in temperature because at elevated temperature increase in  $K_w$  is greater as compared to  $K_a$  and  $K_b$ .

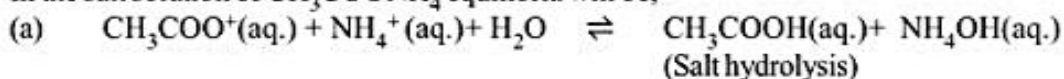
### BUFFER SOLUTIONS

- In certain applications of chemistry and biochemistry solutions of constant pH is required. Such solution are called buffer solution.
- A solution whose pH is not altered to any great extent by the addition of small quantities of either an acid ( $H^+$  ions) or a base ( $OH^-$  ions) is called buffer solution.
- Buffer solutions are also called solutions of reverse acidity or alkalinity.
- Characteristics of buffer solutions
  - (a) It must have constant pH.
  - (b) Its pH should not be changed on long standing
  - (c) Its pH should not be changed on dilution.
  - (d) Its pH should not be changed to any great extent on addition of small quantity of acid or base.
- Buffer solutions can be classified as follows.
  - (A) Simple buffer
  - (B) Mixed buffer

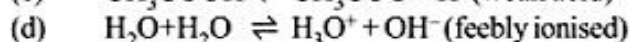
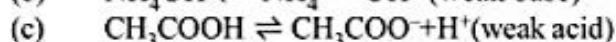
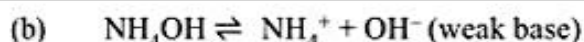
#### A. Simple buffer

- (i) It is a solution of one compound (salts of WA + WB)
- (ii) Buffer action of such solution can be explained as follows-

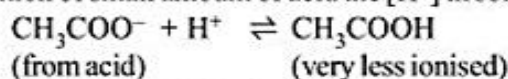
In the salt solution of CH<sub>3</sub>COONH<sub>4</sub> equilibria will be,



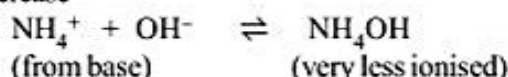




on addition of small amount of acid the  $[\text{H}^+]$  in solution will increase and



equilibria will shift in forward direction. Similarly on addition of small amount of base, the  $[\text{OH}^-]$  in solution will increase



equilibria will shift in forward direction. Hence one can conclude that there will be no change (almost) in the pH of the solution.

(iii) Simple buffer solutions have very little significance since

$$\text{pH} = 7 + \frac{1}{2} \text{pK}_a - \frac{1}{2} \text{pK}_b$$

so solution of desired pH can not be prepared.

## B. Mixed buffer

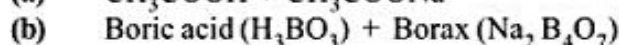
Mixed buffers are solutions of more than one compounds. They can be further classified as

- (a) Acidic buffer                      (b) Basic buffer

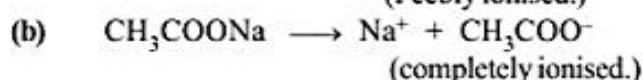
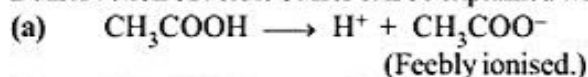
### 1. Acidic buffer

(i) These are the mixture of a weak acid and its salt with strong base.

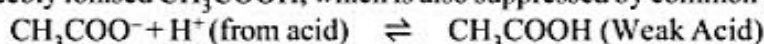
e.g.



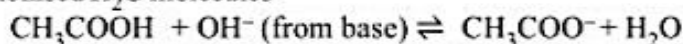
(ii) Buffer action of acidic buffer can be explained with following equilibria,



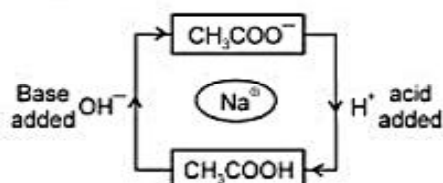
When a strong acid is added in the solution  $[\text{H}^+]$  increases, which will combine with  $\text{CH}_3\text{COO}^-$  to form feebly ionised  $\text{CH}_3\text{COOH}$ , which is also suppressed by common ion effect,



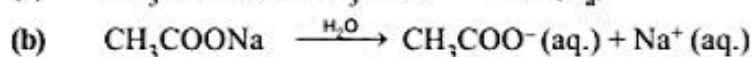
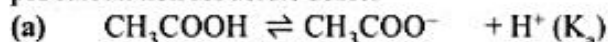
Again when strong base is added in the solution it will attack on unionised acid  $\text{CH}_3\text{COOH}$  to form feebly ionised  $\text{H}_2\text{O}$  molecules



(iii) One can remember, buffer action of acidic buffer with the help of following figure -



(iv) pH calculation for acidic buffer



$\text{CH}_3\text{COOH}$  is feebly ionised and its ionisation is also suppressed by presence of common ion ( $\text{CH}_3\text{COO}^-$ ).



So one can fairly assume  $[CH_3COO^-] = [\text{salt}]$  and  $[CH_3COOH] = [\text{Acid}]$  taken initially in buffer solution.

$$\text{so} \quad K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$$

$$\text{or} \quad [H^+] = \frac{K_a[CH_3COOH]}{[CH_3COO^-]}$$

$$\log[H^+] = \log K_a + \log[CH_3COOH] - \log[CH_3COO^-]$$

$$-\log[H^+] = -\log K_a - \log[CH_3COOH] + \log[CH_3COO^-]$$

$$pH = pK_a + \log \frac{[CH_3COO^-]}{[CH_3COOH]}$$

$$pH = pK_a + \log \frac{[\text{Conjugate base}]}{[\text{Acid}]}$$

$$\text{or} \quad pH = pK_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

Above equation is called Henderson's equation.

**Note :**

- If we increase the concentration of given salt in acidic buffer, pH will also increases.
- If we increase the concentration of acid in acidic buffer, pH will decreases.
- If conc. and volume are given for salt and acid then the pH is given by the following formula-

$$pH = pK_a + \log \frac{[N_2V_2]}{[N_1V_1]}$$

Where  $N_2V_2$  = conc. & volume of salt

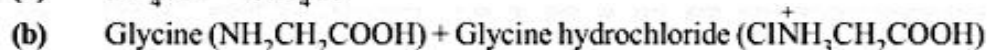
$N_1V_1$  = conc. & volume of acid

- Mixture of weak acid and strong base solution can also act as an acidic buffer, if value of  $N_1V_1$  of weak acid is greater than the value of  $N_2V_2$  of strong base.

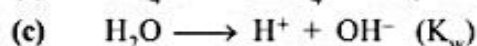
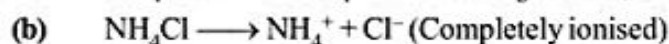
## 2. Basic Buffer

- (i) These are the mixture of a weak base and its salt with strong acid.

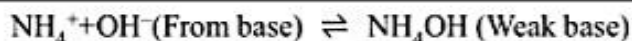
e.g.



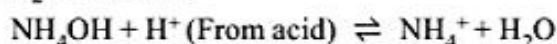
- (ii) Buffer action of basic buffer can be explained with the help of following equilibria



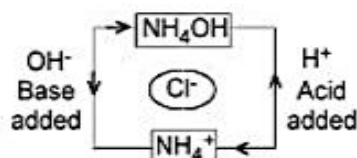
When a strong base is added in the solution  $[OH^-]$  increases, which will combine with  $NH_4^+$  to form feebly ionised  $NH_4OH$ , which is also suppressed by common ion effect.



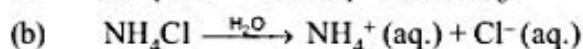
Again when strong acid is added in the solution it will attack on unionised base  $\text{NH}_4\text{OH}$  to form feebly ionised  $\text{H}_2\text{O}$  molecules.



- (iii) One can remember the buffer action of basic buffer with the help of following figure -



- (iv) pH of such basic buffer can be calculated from Henderson - equation as follows.



$\text{NH}_4\text{OH}$  is feebly ionised and its ionisation is also suppressed by presence of common ion ( $\text{NH}_4^+$ ).

So one can fairly assume  $[\text{NH}_4^+] = [\text{Salt}]$  and  $[\text{NH}_4\text{OH}] = [\text{Base}]$  taken initially in buffer solution.

$$\text{so} \quad K_b = \frac{[\text{OH}^-][\text{NH}_4^+]}{[\text{NH}_4\text{OH}]}$$

$$\text{or} \quad [\text{OH}^-] = \frac{K_b[\text{NH}_4\text{OH}]}{[\text{NH}_4^+]}$$

$$= \frac{K_b[\text{Base}]}{[\text{Salt}]}$$

$$\text{or} \quad \text{pOH} = \text{p}K_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

$$\text{or} \quad \text{pH} = 14 - \text{pOH}$$

### 3. Buffer Capacity

- (i) The property of a buffer solution to resist alteration in its pH value is known as buffer capacity.  
 (ii) Buffer capacity is number of moles of acid or base added in one litre of solution so as to change the pH by unity, i.e.

$$\text{Buffer capacity } (\phi) = \frac{\text{Number of moles of acid or base added 1litre solution}}{\text{Change in pH}}$$

- (iii) Higher the buffer capacity, better will be the buffer solution  
 (iv) For maximum buffer capacity of a given buffer concentration of salt should be equal to the concentration acid/base  
 (v) A buffer solution work in a buffer range from  $\text{pH} = \text{p}K_a \pm 1$   
 (vi) A buffer solution work between  $0.1 < \frac{[\text{Salt}]}{[\text{Acid/ Base}]} < 10$

**Illustration**

1. What will be the pH of the buffer solution containing 0.15 moles of  $\text{NH}_4\text{OH}$  and 0.25 moles of  $\text{NH}_4\text{Cl}$ .  $K_b$  for  $\text{NH}_4\text{OH}$  is  $1.8 \times 10^{-5}$ .

(A) 9.08 (B) 10.03 (C) 9.05 (D) 9.03

**Ans. D**

**Sol.** Since it is a basic buffer so,

$$\text{pOH} = \text{p}K_b + \log[\text{Salt}]/[\text{Base}]$$

$$\begin{aligned}\text{pOH} &= -\log K_b + \log[\text{Salt}/\text{Base}] \\ &= -\log(1.8 \times 10^{-5}) + \log(0.25/0.15) \\ &= 4.74 + 0.22 = 4.96\end{aligned}$$

$$\text{or pOH} = 4.97$$

$$\begin{aligned}\text{pH} &= 14 - \text{pOH} \\ &= 14 - 4.97 = 9.03\end{aligned}$$

2. Calculate the pH of a buffer prepared by mixing 300 cc of 0.3 M  $\text{NH}_3$  and 500 cc of 0.5 M  $\text{NH}_4\text{Cl}$ .  $K_b$  for  $\text{NH}_3 = 1.8 \times 10^{-5}$ —

(A) 8.11 (B) 9.81 (C) 8.82 (D) None of these

**Ans. C**

**Sol.** Total volume of the buffer solution

$$= 300 \text{ cc} + 500 \text{ cc} = 800 \text{ cc}$$

$$\text{Number of milli moles of } \text{NH}_3 = 300 \times 0.3 = 90$$

$$\text{Molarity of } \text{NH}_3 \text{ (Base) in the buffer} = 90/800 \text{ M}$$

$$\text{Number of milli moles of } \text{NH}_4\text{Cl} = 500 \times 0.5 = 250.0$$

$$\text{Molarity of [salt] in the buffer} = 250/800 \text{ M}$$

Henderson's equation for basic buffer is:

$$\begin{aligned}\text{pOH} &= -\log K_b + \log \frac{[\text{Salt}]}{[\text{Base}]} \\ &= -\log 1.8 \times 10^{-5} + \log \frac{250/800}{90/800} \\ &= 4.74 + \log 250/90 \\ &= 4.74 + 0.44 \\ &= 5.18 \\ \text{pH} &= 14 - \text{pOH} = 14 - 5.18 = 8.82\end{aligned}$$

3. Calculate the pH of a buffer solution prepared by dissolving 10.6 g of  $\text{Na}_2\text{CO}_3$  in 500 ml of an aqueous solution containing 80 ml of 1M HCl. ( $K_a$  for  $\text{HCO}_3^- = 6 \times 10^{-11}$ )

(A) 8.6 (B) 9.6 (C) 11.6 (D) 12.6

**Ans. B**

**Sol.**

	$\text{Na}_2\text{CO}_3$	+	HCl	→	NaCl	+	$\text{NaHCO}_3$
Meq. before	$\frac{10.6}{106} \times 1000$		$80 \times 1$		0		0
Reaction =	100		80		0		0
Meq. After	20		0		80		80

Reaction

The solution  $\text{Na}_2\text{CO}_3$  and  $\text{HCO}_3^-$  and thus acts as buffer

$$\text{pH} = -\log K_a + \log \frac{[\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = -\log 6 \times 10^{-11} + \log \frac{20}{80} = 9.6$$

4. The concentration of  $\text{H}^+$  ion in a 0.2 M solution of  $\text{HCOOH}$  is  $6.4 \times 10^{-3} \text{ mole L}^{-1}$ . To this solution  $\text{HCOONa}$  is added so as to adjust the concentration of  $\text{HCOONa}$  to one mole per litre. What will be the pH of this solution?  $K_a$  for  $\text{HCOOH}$  is  $2.4 \times 10^{-4}$  and the degree of dissociation of  $\text{HCOONa}$  is 0.75

(A) 3.19 (B) 4.19 (C) 5.19 (D) 6.19

Ans. B

Sol. Assuming that the addition of  $\text{HCOONa}$  suppresses the ionization of  $\text{HCOOH}$ , we can use the expression

$$\text{pH} = \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

to compute pH of the solution, since salt is 75% dissociated we will get,

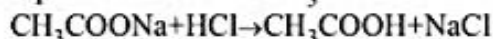
$$\begin{aligned} \text{pH} &= -\log(2.4 \times 10^{-4}) + \log \frac{0.75}{0.2} \\ &= 3.62 + 0.57 = 4.19 \end{aligned}$$

5. Calculate the ratio of pH of a solution containing 1 mole of  $\text{CH}_3\text{COONa}$  + 1 mole of  $\text{HCl}$  per litre and of other solution containing 1 mole  $\text{CH}_3\text{COONa}$  + 1 mole of acetic acid per litre.

(A) 1 : 1 (B) 2 : 1 (C) 1 : 2 (D) 2 : 3

Ans. C

Sol. Case I - pH when 1 mole  $\text{CH}_3\text{COONa}$  and 1 mole  $\text{HCl}$  are present



Before reaction	1	1	0	0
After reaction	0	0	1	1

$$[\text{CH}_3\text{COOH}] = 1\text{M}$$

$$\therefore [\text{H}^+] C_\alpha = C \cdot \sqrt{\frac{K_a}{C}} = \sqrt{C \cdot K_a} = \sqrt{K_a}$$

$$\therefore C = 1$$

$$\therefore \text{pH}_1 = -\frac{1}{2} \log K_a$$

Case II - pH when 1 mole  $\text{CH}_3\text{COONa}$  and 1 mole of  $\text{CH}_3\text{COOH}$ , a buffer solution

$$\therefore \text{pH}_2 = -\log K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} = -\log K_a \quad \therefore [\text{Salt}] = [\text{Acid}] = 1\text{M}$$

$$\therefore \frac{\text{pH}_1}{\text{pH}_2} = \frac{1}{2} \text{ or } \text{pH}_1 : \text{pH}_2 = 1 : 2$$



6. In which case pH will not change on dilution  
 (A) 0.01 M  $\text{CH}_3\text{COONa}$  + 0.01 M  $\text{CH}_3\text{COOH}$  buffer  
 (B) 0.01 M  $\text{CH}_3\text{COONH}_4$   
 (C) 0.01 M  $\text{NaH}_2\text{PO}_4$   
 (D) in all cases

Ans. (D)

Sol. Mixture of Sodium acetate and acetic acid is a buffer of pH value equal to  $\text{p}K_a$  so its buffer capacity is maximum and hence its pH will not change significantly while  $\text{CH}_3\text{COONH}_4$  is a salt of weak acid  $\text{CH}_3\text{COOH}$  and weak base  $\text{NH}_4\text{OH}$  whose magnitude of  $K_a$  and  $K_b$  are equal. So its pH does not depend upon concentration. Further more,  $\text{NaH}_2\text{PO}_4$  is, in fact, a single solute buffer.

### Exercise

1. Calculate pH of the buffer solution containing 0.15 moles of  $\text{NH}_4\text{OH}$  and 0.25 moles of  $\text{NH}_4\text{Cl}$ .  $K_b$  for  $\text{NH}_4\text{OH}$  is  $1.98 \times 10^{-5}$ .  
 (A) 7.034 (B) 9.04 (C) 8.043 (D) None of these

Ans. B

2. What volume of 0.1 M  $\text{HCOONa}$  solution should be added to 50 ml of 0.05 M formic acid to produce a buffer solution of pH = 4.0,  $\text{p}K_a$  of formic acid = 3.7  
 (A) 50 ml (B) 40 ml (C) 30 ml (D) 60 ml

Ans. A

3. What amount of HCl will be required to prepare one litre of a buffer solution (containing NaCN and HCN) of pH 10.4 using 0.01 mole of NaCN. Given  $K_{\text{ion}}(\text{HCN}) = 4.1 \times 10^{-10}$  –  
 (A)  $8.55 \times 10^{-3}$  mole (B)  $8.65 \times 10^{-3}$  mole  
 (C)  $8.75 \times 10^{-3}$  mole (D)  $9.9 \times 10^{-4}$  mole

Ans. D

4. 20 ml of 0.2 M NaOH is added to 50 ml, of 0.2 M  $\text{CH}_3\text{COOH}$  to give 70ml, of the solution. What is the pH of the solution? The ionization constant of acetic acid is  $2 \times 10^{-5}$  –  
 (A) 4.522 (B) 5.568 (C) 6.522 (D) 7.568

Ans. A

### SOLUBILITY (S)

At a constant temperature, the mass of a solute or electrolyte dissolved in the 100 gm of solvent in its saturated solution is called solubility.

Or

Number of gm mole of a solute dissolved in one litre of water at constant temperature is called solubility of that solute.

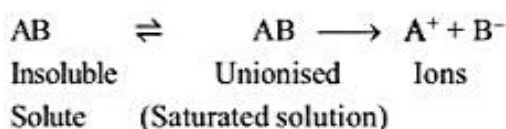
Solubility of a solute in moles / litre

$$= \frac{\text{Solubility of solute in gm / litre}}{\text{molecular weight of the solute}}$$

**1. Solubility product ( $K_{sp}$ ):**

It is the product of the ionic concentration of the ions of binary solid electrolyte in saturated state at constant temperature.

- (a) Let solubility of a compound  $A_x B_y$  be  $s$  moles  $L^{-1}$  it means that if more than  $s$  moles are dissolved in solvent (one litre) only  $s$  moles will be soluble, rest will be insoluble, following equilibrium is established,



**Note :** In the solubility  $s$  moles  $L^{-1}$ , moles of only unionised are counted moles of ions and insoluble solute do not have anything to do.

- (b) According to law of mass action -

$$K_1 = \frac{[A^+][B^-]}{[AB]}$$

$$\text{or} \quad K_1 [AB] = [A^+][B^-] = K_{sp}$$

$K_{sp}$  is called **solubility product**.

- (c) At a certain temperature solubility product of a compound is constant, it means that ions are formed in the manner that product of their concentration is always a constant. However, it becomes clear that if one of ions ( $A^+$  or  $B^-$ ) is added from outside, it would tend to increase  $K_{sp}$  because  $[A^+]$  or  $[B^-]$  has increased, so that extra ions will react with other ions to convert into insoluble part and it precipitates.
- (d)  $K_{sp}$  increases with increase in temperature.
- (e) In a saturated solution.

$$K_{sp} = [A^+][B^-]$$

- (f) In an unsaturated solution of AB

$$K_{sp} > [A^+][B^-]$$

i.e. more solute can be dissolved.

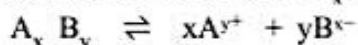
- (g) In a supersaturated solution

$$K_{sp} < [A^+][B^-]$$

i.e. precipitation will start to occur.

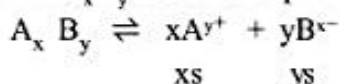
**2. Relationship between Solubility and Solubility Product :**

The equilibrium for a saturated solution of a salt  $A_x B_y$  may be expressed as,



Thus, solubility product  $K_{sp} = [A^{y+}]^x [B^{x-}]^y$

Let the solubility of the salt  $A_x B_y$  in water at a particular temperature be ' $s$ ' moles per litre then

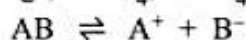


$$\begin{aligned} \text{So,} \quad K_{sp} &= [xs]^x [ys]^y \\ K_{sp} &= x^x \cdot y^y (s)^{x+y} \end{aligned}$$

### S & $K_{sp}$ Relations

#### (a) 1 : 1 types salts or AB type of salts :

eg.  $\text{AgCl}$ ,  $\text{AgI}$ ,  $\text{BaSO}_4$ ,  $\text{PbSO}_4$ , etc.



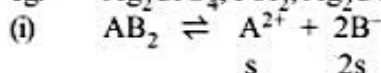
let the solubility of AB is  $s$  moles per litre.

$$\text{So, } K_{sp} = [\text{A}^+][\text{B}^-] = s \times s = s^2$$

$$s = \sqrt{K_{sp}}$$

#### (b) 1 : 2 or 2 : 1 type of salts or $\text{AB}_2$ or $\text{A}_2\text{B}$ type of salts :

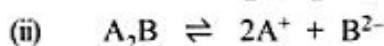
eg.  $\text{Ag}_2\text{CrO}_4$ ,  $\text{PbI}_2$ ,  $\text{Ag}_2\text{CO}_3$ ,  $\text{CaF}_2$ ,  $\text{CaCl}_2$  etc.



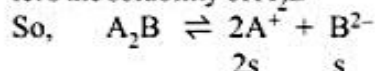
let the solubility of  $\text{AB}_2$  is ' $s$ ' moles per litre

$$\text{So, } K_{sp} = [\text{A}^{2+}][\text{B}^-]^2 = s \times (2s)^2 = 4s^3$$

$$s = \left[ \frac{K_{sp}}{4} \right]^{1/3}$$



let  $s$  the solubility of  $\text{A}_2\text{B}$



$$K_{sp} = [\text{A}^+]^2 [\text{B}^{2-}] = (2s)^2 (s) = 4s^3$$

$$s = \left[ \frac{K_{sp}}{4} \right]^{1/3}$$

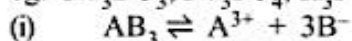
#### (c) 1 : 3 type of salts or salts of $\text{AB}_3$ or $\text{A}_3\text{B}$ type of salt -

$\text{AB}_3 = \text{Valency of A} = 3 \times \text{Valency of B}$

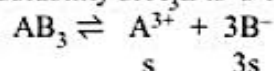
eg.  $\text{FeCl}_3$ ,  $\text{AlCl}_3$ ,  $\text{PCl}_3$ ,  $\text{Al}(\text{OH})_3$ ,  $\text{Fe}(\text{OH})_3$  etc.

$\text{A}_3\text{B} = 3 \times \text{Valency of A} = \text{Valency of B}$

eg.  $\text{Na}_3\text{BO}_3$ ,  $\text{Na}_3\text{PO}_4$ ,  $\text{H}_3\text{PO}_4$  etc.

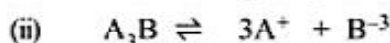


let the solubility of  $\text{AB}_3$  is ' $s$ ' mole / litre.

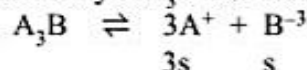


$$K_{sp} = [\text{A}^{3+}][\text{B}^-]^3 = s \times (3s)^3 = 27s^4$$

$$s = \left[ \frac{K_{sp}}{27} \right]^{1/4}$$



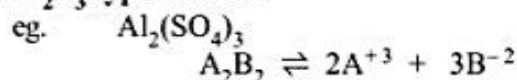
let the solubility of  $\text{A}_3\text{B}$  is ' $s$ ' moles/litre.



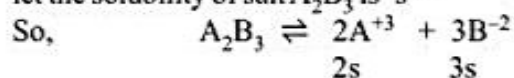
$$K_{sp} = [\text{A}^+]^3 [\text{B}^{3-}] = (3s)^3 \times s = 27s^4$$

$$s = \left[ \frac{K_{sp}}{27} \right]^{1/4}$$

(d) 2 : 3 or  $A_2B_3$  type of salts :



let the solubility of salt  $A_2B_3$  is 's' -



$$K_{sp} = [A^{+3}]^2 [B^{-2}]^3$$

$$= (2s)^2 \times (3s)^3 = 4s^2 \times 27s^3$$

$$K_{sp} = 108 s^5 \quad s = \left[ \frac{K_{sp}}{108} \right]^{1/5}$$

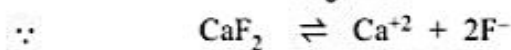
### Illustration

1. The solubility of  $CaF_2$  in water at  $20^\circ C$  is 15.6 mg per  $dm^3$  solution. What will be the solubility product of  $CaF_2$  -

- (A)  $4.0 \times 10^{-4}$  (B)  $8.0 \times 10^{-8}$  (C)  $32.0 \times 10^{-12}$  (D) None

Ans. C

Sol. Solubility in moles per  $dm^3 = \frac{15.6 \times 10^{-3}}{78 \text{ g/mole}} = 2.0 \times 10^{-4}$



$$\therefore [Ca^{+2}] = 2.0 \times 10^{-4}$$

$$\text{and } [F^-] = 2 \times 2.0 \times 10^{-4}$$

Hence, solubility product  $K_{sp}$

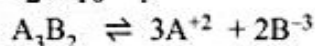
$$= [Ca^{+2}] [F^-]^2 = [2.0 \times 10^{-4}] [4.0 \times 10^{-4}]^2 = 32 \times 10^{-12}$$

2. Given the solubility product of  $F_3B_2$  is  $2 \times 10^{-30}$ . What will be the solubility in moles/litre.

- (A)  $(1.85 \times 10^{-32})^{1/5}$  (B)  $\left( \frac{2 \times 10^{-30}}{108} \right)^{1/5}$  (C)  $\left( \frac{2 \times 10^{-28}}{5400} \right)^{1/5}$  (D) All

Ans. B

Sol.  $K_{sp}$  of  $A_3B_2 = 2 \times 10^{-30}$ .



Assume s is the solubility of  $A_3B_2$

$$\text{then } K_{sp} = (3s)^3 (2s)^2 = 108 s^5$$

$$s = 5 \sqrt[5]{\frac{K_{sp}}{108}} \quad s = \left( \frac{2 \times 10^{-30}}{108} \right)^{1/5}$$

### Exercise

1. How many milligrams of  $AgBr$  will dissolve in water to give litres of aqueous solution. Given  $K_{sp}$  for  $AgBr$  (Mol. wt. 188) =  $5.0 \times 10^{-13} M^2$  -

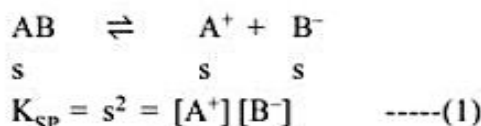
- (A)  $7.071 \times 10^{-7}$  moles per litre (B)  $70.71 \times 10^{-7}$  moles per litre  
 (C)  $707.1 \times 10^{-7}$  moles per litre (D) None of these

Ans. A

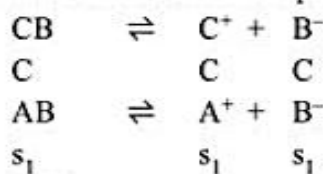


**1. Effect of Common ion on Solubility :**

As we saw that for a saturated solution product of concentration of ions should not exceed a constant called solubility product. Now suppose, extra common ions are added to increase concentration of ions it will tend to increase the value of  $K_{sp}$ , but it can not increase so ions will react to form molecule and get precipitated e.g. let solubility of AB in water be  $s$  moles  $L^{-1}$ . It is dissolved in solution CB having a common ion  $B^{-}$  let concentration of CB be  $C$ .



(Product should not exceed  $s^2$  otherwise precipitation will start) Now. Let solubility of AB in CB be  $S_1$ .



$$[A^{+}] = s_1$$

$$[B^{-}] = s_1 + C$$

$$K_{sp} = (s_1)(s_1 + C)$$

If  $s_1 \lll C$

$$K_{sp} = s_1 C = s^2, \text{ from equation (1)}$$

or 
$$s_1 = \frac{s^2}{C}$$

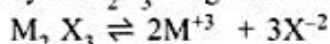
So, solubility gets reduced.

**Illustration**

1. A salt  $M_2X_3$  dissolves in water such that its solubility is  $x$  g. mole/litre. Its  $K_{sp}$  is –  
 (A)  $x^5$  (B)  $6x^2$  (C)  $108 x^5$  (D)  $6x^5$

**Ans. C**

**Sol.** Solubility of  $M_2X_3 = x$  gm mole/litre



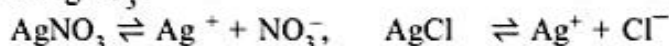
$$\therefore [M^{+3}] = 2x, \quad [X^{-2}] = 3x$$

$$\text{Solubility product } K_{sp} = (2x)^2 \cdot (3x)^3 = 108 x^5$$

2. Solubility product of AgCl is  $2.8 \times 10^{-10}$  at  $25^\circ C$ . Calculate solubility of the salt in  $0.1 M AgNO_3$  solution :  
 (A)  $2.8 \times 10^{-9}$  mole/litre (B)  $2.8 \times 10^{-10}$  mole/litre  
 (C)  $3.2 \times 10^{-9}$  mole/litre (D)  $3.2 \times 10^{-12}$  mole/litre

**Ans. A**

**Sol.** In  $0.1 M AgNO_3$



$$K_{sp} = [Ag^{+}][Cl^{-}]$$

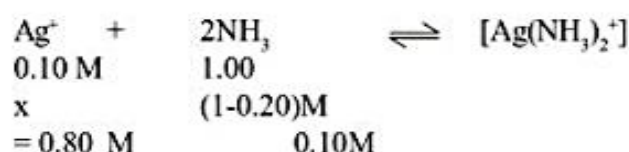
Now  $[Ag^{+}]$  can be taken as  $[AgNO_3]$

while  $[Cl^{-}]$  is the solubility of AgCl

$$\therefore Cl = \frac{K_{sp}}{[Ag^{+}]} = \frac{2.8 \times 10^{-10}}{0.1} \quad \therefore \text{Solubility of AgCl} = 2.8 \times 10^{-9} \text{ mole/litre}$$

3. 0.10 mol sample of  $\text{AgNO}_3$  is dissolved in one litre of 1.00 M  $\text{NH}_3$ . If 0.010 mol of  $\text{NaCl}$  is added to this solution will  $\text{AgCl(s)}$  Precipitate?

Sol.  $K_{sp}(\text{AgCl}) = 1.8 \times 10^{-10}$ ,  $K_f[\text{Ag}(\text{NH}_3)_2]^+ = 1.6 \times 10^7$



It is assumed than all  $\text{Ag}^+$  ion has been complexed and only its part x is left

$$K_f = \frac{[\text{Ag}(\text{NH}_3)_2]^+}{[\text{Ag}^+][\text{NH}_3]^2} \Rightarrow 1.6 \times 10^7 = \frac{0.10}{x(0.80)^2}$$

$$\therefore x = 9.8 \times 10^{-9} \text{ M} = [\text{Ag}^+] \text{ undissolved}$$

$$[\text{Cl}^-] = 1.0 \times 10^{-2} \text{ M}$$

$$\therefore [\text{Ag}^+][\text{Cl}^-] = 9.8 \times 10^{-9} \times 1.0 \times 10^{-2} = 9.8 \times 10^{-11} < 1.8 \times 10^{-10} (K_{sp}(\text{AgCl}))$$

Hence  $\text{AgCl(s)}$  will not precipitate.

4. What is the minimum concentration of  $\text{NH}_3$  required to prevent  $\text{AgCl(s)}$  from precipitating from 1.00 litre of a solution containing 0.10 mol of  $\text{AgNO}_3$  and 0.010 mol  $\text{NaCl}$ ?

$$K_{sp}(\text{AgCl}) = 1.8 \times 10^{-10}$$

$$K_f[\text{Ag}(\text{NH}_3)_2]^+ = 1.6 \times 10^7$$

Sol. In order to prevent precipitation of  $\text{AgCl}$

$$[\text{Ag}^+][\text{Cl}^-] \leq K_{sp}$$

$$\Rightarrow [\text{Ag}^+](0.01) \leq 1.8 \times 10^{-10}, \text{ As } [\text{Cl}^-] = 0.01 \text{ M}$$

$$\therefore [\text{Ag}^+] \leq 1.8 \times 10^{-8} \text{ M}$$

The maximum concentration of free uncomplexed  $\text{Ag}^+$  permitted in the solution is  $1.8 \times 10^{-8}$ . That is almost all  $\text{Ag}^+$  (0.10M) must be complexed



$$[\text{NH}_3] = ?, \quad [\text{Ag}^+] = 1.8 \times 10^{-8} \text{ M.}$$

$$[\text{Ag}(\text{NH}_3)_2]^+ = 0.10 \text{ M}$$

$$K_f = \frac{[\text{Ag}(\text{NH}_3)_2]^+}{[\text{Ag}^+][\text{NH}_3]^2} \Rightarrow 1.6 \times 10^7 = \frac{0.10}{(1.8 \times 10^{-8})[\text{NH}_3]^2}$$

$$\therefore [\text{NH}_3]^2 = 0.3472 \Rightarrow [\text{NH}_3] = 0.589 \text{ M}$$

The concentration calculated above is that of free uncomplexed  $\text{NH}_3$ .  $[\text{NH}_3]$  required by

$$0.1 \text{ M Ag}^+ \text{ in the formation of } [\text{Ag}(\text{NH}_3)_2]^+ = 0.2 \text{ M}$$

$$\text{Hence } [\text{NH}_3]_{\text{total}} = 0.2 + 0.589 = 0.789 \text{ M}$$

### Exercise

1. The solubility product of chalk is  $9.3 \times 10^{-8}$ . Calculate its solubility in gram per litre –  
(A) 0.3040 gram/litre (B) 0.0304 gram/litre (C) 2.0304 gram/litre (D) 4.0304 gram/litre

Ans. B

2. Given  $\text{Ag}^+ (\text{NH}_3)_2 \rightleftharpoons \text{Ag}^+ + 2\text{NH}_3$ ,  $K_c = 6.2 \times 10^{-8}$  and  $K_{sp}(\text{AgCl}) = 1.8 \times 10^{-10}$  at 298 K. Calculate the concentration of complex in 1.0 M aqueous ammonia.

Ans.  $[\text{Ag}(\text{NH}_3)_2] = 0.539$ .

### 3. Applications of $K_{sp}$ :

- A. **In purification of common salt :** In a saturated solution of NaCl & impurities, by passing HCl gas through it, increase the  $\text{Cl}^-$  ion concentration which shifts the equilibrium  $\text{NaCl} \rightleftharpoons \text{Na}^+ + \text{Cl}^-$  to left & causes the precipitation of NaCl.
- B. **In preparation of  $\text{NaHCO}_3$  by solvay method :** Precipitation of  $\text{NaHCO}_3$  from its saturated solution is done by addition of  $\text{NH}_4\text{HCO}_3$ ,  $\text{HCO}_3^-$  as common ion.
- C. **Predicting precipitation in ionic reactions :** Precipitation in an ionic reactions could be predicted by comparing  $K_{sp}$  to the ionic concentration product of ions.
- D. **Salting out action of Soap :** When NaCl is added to saturated solution of soap ( $\text{RCOONa}$ ) concentration of  $\text{Na}^+$  increases & causes to precipitation of soap, it is due to  $[\text{Na}^+][\text{RCOO}^-] > K_{sp}$ .
- E. **In qualitative analysis :** Selective precipitation of salt in salt analysis due to suppression of common ion.

## THEORY OF INDICATORS

An indicator is a substance which is used to determine the end point in a titration. In acid-base titrations, organic substances (weak acids or weak bases) are generally used as indicators. They change their colour within a certain pH range. The colour change and the pH range of some common indicators are tabulated below:

Indicator	pH range	Colour change
Methyl orange	3.2-4.5	Pink to yellow
Methyl red	4.4-6.5	Red to yellow
Litmus	5.5-7.5	Red to blue
Phenol red	6.8-8.4	Yellow to red
Phenolphthalein	8.3-10.5	Colourless to pink

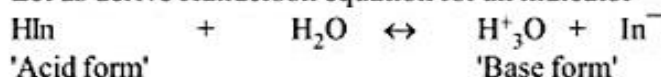
*Theory of acid-base indicators: Two theories have been proposed to explain the change of colour of acid-base indicators with change in pH.*



### 1. Ostwald's Theory

- The colour change is due to ionisation of the acid-base indicator. The unionised form has different colour than the ionised form.
- The ionisation of the indicator is largely affected in acids and bases as it is either a weak acid or a weak base. In case, the indicator is a weak acid, its ionisation is very much low in acids due to common  $H^+$  ions while it is fairly ionised in alkalies. Similarly if the indicator is a weak base, its ionisation is large in acids and low in alkalies due to common  $OH^-$  ions.

Let us derive Handerson equation for an indicator



### Conjugate acid-base pair

$$\begin{aligned} K_{\text{In}} &= [\text{In}][\text{H}_3\text{O}^+]/[\text{HIn}]; & K_{\text{In}} &= \text{Ionization constant for indicator} \\ [\text{H}_3\text{O}^+] &= K_{\text{In}} * [\text{HIn}]/[\text{In}^-] \end{aligned}$$

$$\text{pH} = -\log_{10} [\text{H}_3\text{O}^+] = -\log_{10} [K_{\text{In}}] - \log_{10} [\text{HIn}]/[\text{In}^-]$$

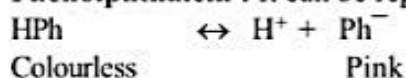
$$\text{pH} = \text{p}K_{\text{In}} + \log_{10} [\text{In}^-]/[\text{HIn}] \quad (\text{Handerson equation for indicator})$$

At equivalence point

$$[\text{In}^-] = [\text{HIn}] \quad \text{and} \quad \text{pH} = \text{p}K_{\text{In}}$$

### Working principle of phenolphthalein & methyl orange indicators :

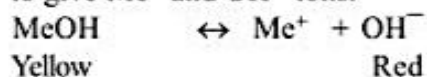
- Phenolphthalein** : It can be represented as HPh. It ionises in solution to a small extent as:



$$K = [\text{H}^+] [\text{Ph}^-] / [\text{HPh}]$$

*The undissociated molecules of phenolphthalein are colourless while  $\text{Ph}^-$  ions are pink in colour. In presence of an acid the ionisation of HPh is practically negligible as the equilibrium shifts to left hand side due to high concentration of  $\text{H}^+$  ions. Thus, the solution would remain colourless. On addition of alkali, hydrogen ions are removed by  $\text{OH}^-$  ions in the form of water molecules and the equilibrium shifts to right hand side. Thus, the concentration of  $\text{Ph}^-$  ions increases in solution and they impart pink colour to the solution.*

- Methyl orange** : It is a very weak base and can be represented as MeOH. It is ionized in solution to give  $\text{Me}^+$  and  $\text{OH}^-$  ions.



$$K = [\text{Me}^+] [\text{OH}^-] / [\text{MeOH}]$$

*In presence of an acid,  $\text{OH}^-$  ions are removed in the form of water molecules and the above equilibrium shifts to right hand side. Thus, sufficient  $\text{Me}^+$  ions are produced which impart red colour to the solution. On addition of alkali, the concentration of  $\text{OH}^-$  ions increases in the solution and the equilibrium shifts to left hand side, i.e., the ionisation of MeOH is practically negligible. Thus, the solution acquires the colour of unionised methyl orange molecules, i.e., yellow.*



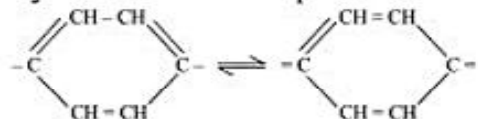
This theory also explains the reason why phenolphthalein is not a suitable indicator for titrating a weak base against strong acid. The  $\text{OH}^-$  ions furnished by a weak base are not sufficient to shift the equilibrium towards right hand side considerably, i.e., pH is not reached to 8.3. Thus, the solution does not attain pink colour. Similarly, it can be explained why methyl orange is not a suitable indicator for the titration of weak acid with strong base.

## 2. Quinonoid theory:

- (a) The acid-base indicators exist in two tautomeric forms having different structures. Two forms are in equilibrium.

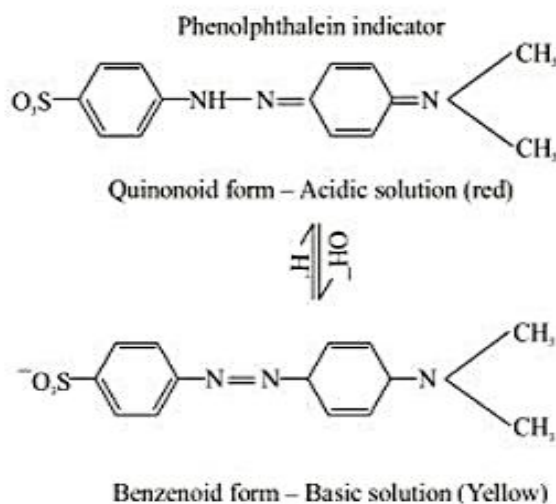
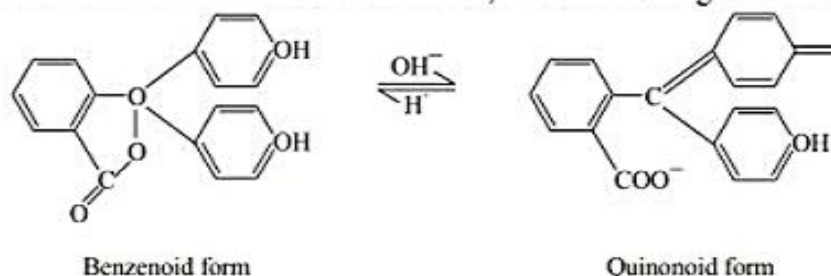
Phenolphthalein has benzenoid form in acidic medium and thus, it is colourless while it has quinonoid form in alkaline medium which has pink colour.

Methyl orange has quinonoid form in acidic solution and benzenoid form in alkaline solution. The color of benzenoid form is yellow while that of quinonoid form is red.



- (b) The two forms have different colors. The color change is due to the inter conversion of one tautomeric form into other.
- (c) One form mainly exists in acidic medium and the other in alkaline medium.

Thus, during titration the medium changes from acidic to alkaline or vice-versa. The change in pH converts one tautomeric form into other and thus, the colour change occurs.



Methyl orange indicator

### Selection of suitable indicator

In order to choose a suitable indicator, it is necessary to understand the pH changes in different types of titrations. The change in pH in the vicinity of the equivalence point is most important for this purpose.

The curve obtained by plotting pH as ordinate against the volume of alkali added as abscissa is known as neutralisation or titration curve.

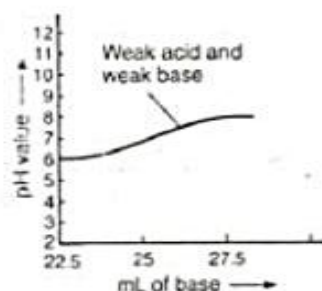
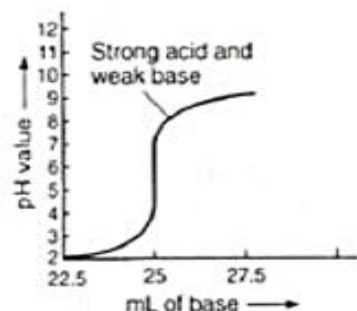
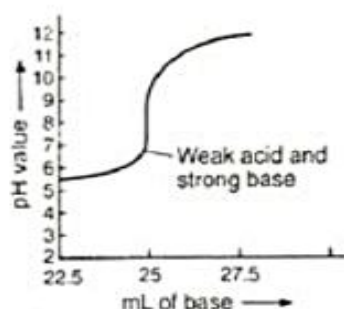
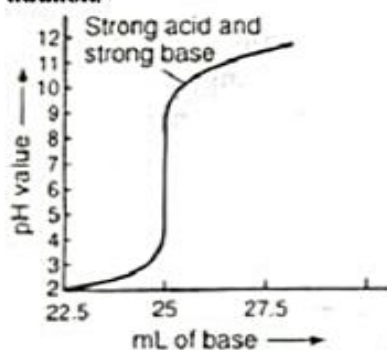
### Types of Neutralisation reaction

#### (i) Strong acid vs. strong base:

pH curve of strong acid (say HCl) and strong base (say NaOH) is vertical over almost the pH range 4-10. So the indicators phenolphthalein (pH range 8.3 to 10.5), methyl red (pH range 4.4-6.5) and methyl orange (pH range 3.2-4.5) are suitable for such a titration.

#### (ii) Weak acid vs. weak base:

pH curve of weak acid (say  $\text{CH}_3\text{COOH}$  of oxalic acid) and strong base (say NaOH) is vertical over the approximate pH range 7 to 11. So phenolphthalein is the suitable indicator for such a titration.



#### (iii) Strong acid vs. weak base:

pH curve of strong acid (say HCl or  $\text{H}_2\text{SO}_4$  or  $\text{HNO}_3$ ) with a weak base (say  $\text{NH}_4\text{OH}$ ) is vertical over the pH range of 4 to 7. So the indicators methyl red and methyl orange are suitable for such a titration.

#### (iv) Weak acid vs. Strong base :

pH curve of weak acid (say  $\text{CH}_3\text{COOH}$ ) with a strong base (say NaOH) is vertical over the pH range 7 to 10. So phenolphthalein is suitable indicator for such titration

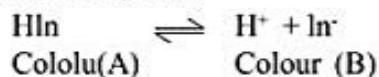
**Illustration**

1. The pH at which an acid indicator with  $K_a = 1 \times 10^{-5}$  changes colours when indicator concentration is  $1 \times 10^{-5}$  M is

(A) 4 (B) 5 (C) 6 (D) 3

Ans. B

Sol. For acid indicator HIn



$$K_{\text{In}} = \frac{[\text{H}^+][\text{In}^-]}{[\text{HIn}]} \text{ when } [\text{In}^-] = [\text{HIn}] \text{ indicator changes colour.}$$

$$\therefore K_{\text{In}} = [\text{H}^+] = 1 \times 10^{-5} \quad \therefore \text{pH} = 5$$

**Exercise**

1. If an acidic indicator HIn ionises as  $\text{HIn} \rightleftharpoons \text{H}^+ + \text{In}^-$ . To which maximum pH value its solution has distinct colour characteristic of HIn.

(A)  $\text{p}K_{\text{In}} - 1$  (B)  $\text{p}K_{\text{In}} \pm 1$  (C)  $\text{p}K_{\text{In}}$  (D) 7

Ans. B

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**SOLVED EXAMPLES**


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**Q.1** For an aqueous solution to be neutral it must have

- (A)  $\text{pH} = 7$                       (B)  $[\text{H}^+] = [\text{OH}^-]$                       (C)  $[\text{H}^+] = \sqrt{K_w}$                       (D)  $[\text{H}^+] < [\text{OH}^-]$

**Ans.** B

**Sol.** For neutral solution  $[\text{H}^+]$  always must be equal to  $[\text{OH}^-]$

**Q.2** If an aqueous solution at  $25^\circ\text{C}$  has twice as many  $\text{OH}^-$  as pure water its  $\text{pOH}$  will be

- (A) 6.699                      (B) 7.307                      (C) 7                      (D) 6.98

**Ans.** A

**Sol.**  $[\text{OH}^-] = 2 \times 10^{-7}$

$$\text{pOH} = 14 - \text{pH} \text{ or } -\log [\text{OH}^-]$$

**Q.3** The  $\text{pH}$  of a solution prepared by mixing 50.0 mL of 0.02 M NaOH and 50 mL of 0.04 M  $\text{CH}_3\text{COOH}$  is ( $K_a = 1.8 \times 10^{-5}$ ).

- (A) 4.74                      (B) 5.74                      (C) 3.74                      (D) 7.45

**Ans.** A

**Sol.** 50 mL of 0.02 M NaOH contains 1 milli moles of  $\text{OH}^-$

50 mL of 0.04 M  $\text{CH}_3\text{COOH}$  contains 2 millimoles of  $\text{H}^+$

The combination of the two solutions will give 1 milli mole of salt, and 1 milli mole of acid will be left behind. By using Henderson equation

$$\text{pH} = \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} \text{ or } \text{pH} = \text{p}K_a + \log \frac{[0.1 \text{ milli mole per } 100 \text{ mL of soln.}]}{[0.1 \text{ milli mole per } 100 \text{ mL of soln.}]}$$

$$\text{Or } \text{pH} = -\log K_a = -\log (1.8 \times 10^{-5}) = 4.74$$

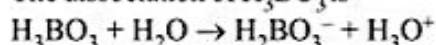
**Q.4** The  $\text{pH}$  of a solution containing 0.10 M  $\text{H}_3\text{BO}_3$  and 0.18 M  $\text{NaH}_2\text{BO}_3$  is

( $K_1 \text{ H}_3\text{BO}_3 = 7.3 \times 10^{-10}$ )

- (A) 7.5                      (B) 12.0                      (C) 9.39                      (D) 10.43

**Ans.** C

**Sol.** The dissociation of  $\text{H}_3\text{BO}_3$  is



$$K_1 = \frac{[\text{H}_2\text{BO}_3^-][\text{H}_3\text{O}^+]}{[\text{H}_3\text{BO}_3]} = \frac{(0.18).x}{(0.10)} = 7.3 \times 10^{-10}$$

$$\text{Or } x = [\text{H}_3\text{O}^+] = 4.1 \times 10^{-10} \text{ or } \text{pH} = -\log x = -\log (4.1 \times 10^{-10}) = 9.39$$

**Q.5** What molar concentration of ammonia will provide a hydroxyl ion concentration of  $1.5 \times 10^{-3}$ ? ( $K_b = 1.8 \times 10^{-5}$ )

- (A) 0.125 M                      (B) 0.12 M                      (C) 0.13 M                      (D) 0.14 M

**Ans.** C

**Sol.** The reaction is  $\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$

$$K_b = 1.8 \times 10^{-5} = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{(1.5 \times 10^{-3})(1.5 \times 10^{-3})}{[\text{NH}_3]} = 1.8 \times 10^{-5}$$


---



Equilibrium conc. of ammonia  $[\text{NH}_3] = 0.125 \text{ M}$

And, total  $[\text{NH}_3] = 1.5 \times 10^{-3} + 0.125 = 0.13 \text{ M}$

- Q.6** A solution of a monoprotic weak acid has acidity constant equal to  $K_a$ . The value of minimum concentration  $C$  in terms of  $K_a$  such that the concentration of undissociated acid can be equated to  $C$  within a limit of error of 10% is

(A)  $C = 10 K_a$  (B)  $C = 0.9 K_a$  (C)  $C = 0.1 K_a$  (D)  $C = 90 K_a$

**Ans.** D

**Sol.** The reaction is  $\text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{A}^-$  and  $K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$

Let  $C$  be the minimum initial concentration and  $x$  the degree of dissociation. Then

$$K_a = \frac{x^2}{C-x}$$

Normally, we make the approximation that  $C-x \sim C$  within an error of 10%.

Therefore,  $C-x = 0.90 C$  or  $x = C-0.90 C = 0.10 C$

$$K_a = \frac{x^2}{C-x} = \frac{(0.10C)^2}{0.90C} = \frac{0.01C^2}{0.90C} = \frac{C}{90} \text{ or } C = 90 K_a$$

- Q.7** If the degree of ionization of water be  $1.8 \times 10^{-9}$  at 298 K. Its ionization constant will be  
(A)  $1.8 \times 10^{-16}$  (B)  $1 \times 10^{-14}$  (C)  $1 \times 10^{-16}$  (D)  $1.67 \times 10^{-14}$

**Ans.** A

**Sol.**  $K_a = \frac{K_w}{[\text{H}_2\text{O}]} = \frac{10^{-14}}{55.5} = 1.8 \times 10^{-16}$

- Q.8** The hydrolysis constant for  $\text{ZnCl}_2$  will be

(A)  $K_h = \frac{K_w}{K_b}$  (B)  $K_h = \frac{K_w^2}{K_b}$  (C)  $K_h = \frac{K_w^2}{K_b^2}$  (D)  $K_h = \frac{K_b}{K_w^2}$

Where  $k_b$  is effective dissociation constant of base  $\text{Zn}^{++}$

**Ans.** B

**Sol.**  $\text{Zn}^{++} + 2\text{H}_2\text{O} \rightleftharpoons \text{Zn(OH)}_2 + 2\text{H}^+$

$$\therefore K_h = \frac{[\text{Zn(OH)}_2][\text{H}^+]^2}{[\text{Zn}^{++}]} \quad \dots (1)$$

$\text{Zn(OH)}_2 \rightleftharpoons \text{Zn}^{++} + 2\text{OH}^-$

$$\therefore K_b = \frac{[\text{Zn}^{++}][\text{OH}^-]^2}{[\text{Zn(OH)}_2]}$$

$$K_w = [\text{H}^+][\text{OH}^-] \therefore \frac{K_w^2}{K_b} = K_h$$

**Q.9** The solubility product of  $\text{Hg}_2\text{I}_2$  is  $1.2 \times 10^{-28}$ . The concentrations of cation and anion in a saturated solution of  $\text{Hg}_2\text{I}_2$  in water is

- (A)  $\text{Hg}_2^{2+} = 3.1 \times 10^{-10} \text{ M}$  and  $\text{I}^- = 6.2 \times 10^{-10} \text{ M}$   
 (B)  $\text{Hg}_2^{2+} = 6.2 \times 10^{-10} \text{ M}$  and  $\text{I}^- = 12.4 \times 10^{-10} \text{ M}$   
 (C)  $\text{Hg}_2^{2+} = 3.1 \times 10^{-14} \text{ M}$  and  $\text{I}^- = 6.2 \times 10^{-14} \text{ M}$   
 (D)  $\text{Hg}_2^{2+} = 3.6 \times 10^{-12} \text{ M}$  and  $\text{I}^- = 1.8 \times 10^{-12} \text{ M}$

**Ans.** A

**Sol.**  $\text{Hg}_2\text{I}_2 \rightleftharpoons \text{Hg}_2^{2+} + 2\text{I}^-$   $K_{sp} = [\text{Hg}_2^{2+}][\text{I}^-]^2 = 1.2 \times 10^{-28}$

Let  $\text{Hg}_2^{2+}$  be  $x$ , then  $\text{I}^- = 2x$

$$1.2 \times 10^{-28} = x \cdot [2x]^2 = 4x^3 \text{ or } x = \left[ \frac{1.2 \times 10^{-28}}{4} \right]^{1/3}$$

$$\text{Or } x = 3.1 \times 10^{-10} \text{ M} = [\text{Hg}_2^{2+}]$$

$$2x = 6.2 \times 10^{-10} \text{ M} = [\text{I}^-]$$

**Q.10**  $\text{Mg}(\text{OH})_2$  has a solubility product equal to  $1.2 \times 10^{-11}$ . A solution contains 0.10 moles of magnesium ions per litre. The maximum pH of the solution from which  $\text{Mg}(\text{OH})_2$  will not precipitate is

- (A) 4.96 (B) 9.04 (C) 12.13 (D) 6.94

**Ans.** B

**Sol.**  $\text{Mg}(\text{OH})_2 \rightleftharpoons \text{Mg}^{2+} + 2\text{OH}^-$   $K_{sp} = 1.2 \times 10^{-11}$

$[\text{OH}^-]$  higher than that contained in a saturated solution will cause precipitation. Therefore, the solution must be at the point of attaining equilibrium and the concentration of ions in solution must be no greater than those required to satisfy the solubility product constant. In this solution,  $[\text{Mg}^{2+}] = 0.10 \text{ M}$  and  $[\text{Mg}^{2+}][\text{OH}^-]^2 = 1.2 \times 10^{-11}$

$$[\text{OH}^-]^2 = \frac{1.2 \times 10^{-11}}{0.10} = 1.2 \times 10^{-10} \text{ or } [\text{OH}^-] = 1.1 \times 10^{-5} \text{ or } \text{pOH} = 4.96$$

$$\text{Or } \text{pH} = 9.04$$

**Q.11** Solubility of  $\text{AgCl}$  in water, 0.01 M  $\text{CaCl}_2$ , 0.01 M  $\text{NaCl}$  and 0.05 M  $\text{AgNO}_3$  are  $S_1$ ,  $S_2$ ,  $S_3$  and  $S_4$  respectively then.

- (A)  $S_1 > S_2 > S_3 > S_4$  (B)  $S_1 > S_3 > S_2 > S_4$  (C)  $S_1 > S_2 = S_3 > S_4$  (D)  $S_1 > S_3 > S_4 < S_2$

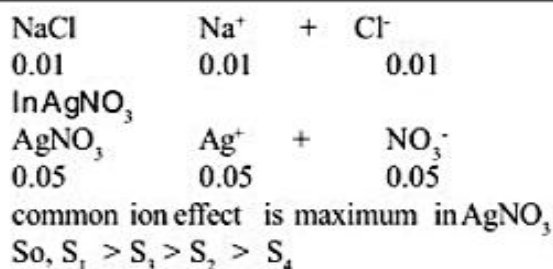
**Ans.** B

**Sol.**  $\text{AgCl} \rightleftharpoons \text{Ag}^+ + \text{Cl}^-$

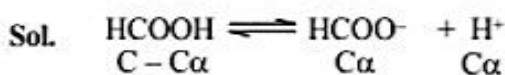
In  $\text{CaCl}_2$

$\text{CaCl}_2 \rightleftharpoons \text{Ca}^{+2} + 2\text{Cl}^-$   
 0.01                      0.01                      2 x 0.01

In  $\text{NaCl}$



**Q.12** Calculate the pH of 0.01 N formic acid solution. The dissociation constant of the acid is  $1.77 \times 10^{-4}$ .



and  $K_a = C\alpha^2$  or  $1.77 \times 10^{-4} = 0.01 \times \alpha^2$

or 
$$\alpha^2 = \frac{1.77 \times 10^{-4}}{0.01} = 1.77 \times 10^{-2}$$

Or  $\alpha = 0.1245 \times 10^{-2}$

Or  $[\text{H}^+] = C\alpha = 1.245 \times 10^{-3}$  and  $\text{pH} = -\log(1.245 \times 10^{-3})$

Or 
$$\begin{aligned} \text{pH} &= -(0.015 - 3.00) = -(-2.905) \\ &= 2.9 \end{aligned}$$

**Q.13** What will be the pH of a solution formed by mixing 40 mL of 0.10 M HCl with 10 mL of 0.45 M NaOH?

**Sol.** 40 mL of 0.1 M HCl =  $\frac{0.1}{1000} \times 40 = 0.004$  moles of HCl

Similarly, 10 mL of 0.45 M NaOH =  $\frac{0.45}{1000} \times 10 = 0.0045$  moles of NaOH

Thus, NaOH left unneutralised = 0.0005 moles in a volume of 50 mL

Concentration of NaOH =  $\frac{1000 \times 0.0005}{50} = 0.01 = 10^{-2}$  M

Therefore,  $[\text{OH}^-] = 10^{-2}$  M or  $[\text{H}^+] = 10^{-12}$  M or  $\text{pH} = 12.0$

**Q.14** A solution of HCl contains 0.1920 g of an acid in 0.5 litre of a solution. The degree of dissociation is 95%. The pH of the solution is ?

**Sol.** Concentration  $C$  of HCl solution =  $\frac{0.1920}{36.5 \times 0.5} = 0.010$  M

The degree of dissociation is 95% i.e., = 0.95

Therefore,  $[\text{H}^+] = 0.010 \times 0.95 = 0.0095$

$$\text{pH} = -\log[\text{H}^+] = -\log(0.0095) = -[\bar{3}.9777] = -(-2.02) = 2.0$$

**Q.15** A solution of acetic acid is 1.0% ionised. Determine the molar concentration of acid ( $K_a = 1.8 \times 10^{-5}$ ) and also the  $[\text{H}^+]$ .



**Sol.**  $\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+$  where 'C' is the concn. of the acid and  $\alpha$  is the degree of dissociation.

$$K_a = 1.8 \times 10^{-5} = C\alpha^2$$

$$\therefore 1.8 \times 10^{-5} = C \cdot (0.01)^2 \text{ or } C = 1.8 \times 10^{-5} \times 10^4 = 1.8 \times 10^{-1} \text{ M}$$

$$[\text{H}^+] = C\alpha \text{ or } [\text{H}^+] = 1.8 \times 10^{-1} \times 0.01 = 0.18 \times 0.01 = 0.0018 \text{ M or } 1.8 \times 10^{-3} \text{ M}$$

**Q.16** A reaction  $\text{CaF}_2 \rightleftharpoons \text{Ca}^{2+} + 2\text{F}^-$  is at equilibrium. If the concentration of  $\text{Ca}^{2+}$  is increased four times, what will be the change in  $\text{F}^-$  concentration as compared to the initial concentration of  $\text{F}^-$ ?

**Sol.** The dissociation constant  $K$  of the reaction  $= \frac{[\text{Ca}^{2+}][\text{F}^-]^2}{[\text{CaF}_2]}$ . When the concentration of  $\text{Ca}^{2+}$  increases and becomes four times, the concentration of  $\text{F}^-$  must decrease by the same value. This is necessary in order to maintain  $K$  as constant. Since the  $\text{F}^-$  concentration is raised to the power 2 in the expression, the concentration of fluoride ion must decrease by  $1/2$ .

**Q.17** An acid solution of  $\text{pH} = 6$  is diluted 1000 times, the  $\text{pH}$  of the final solution is

**Sol.**  $\text{pH} = 6$  means  $[\text{H}^+] = 10^{-6} \text{ M}$ . After dilution, the hydrogen ion concentration becomes  $10^{-9} \text{ M}$ . Under such conditions, the hydrogen ions obtained from water cannot be neglected.

$$\therefore \text{Total } [\text{H}^+] = 10^{-9} + 10^{-7} \text{ (approx.)}$$

$$= 10^{-7} (10^{-2} + 1)$$

$$= 10^{-7} (1.01)$$

[The contribution of  $\text{H}^+$  from water will not be exactly  $10^{-7}$  but still we can make an approximation in an objective problem and take it as  $10^{-7}$ ]

$$\text{pH} = -\log [\text{H}^+] = -1.01 \times 10^{-7}$$

$$= 7 - 0.0043 = 6.9957$$

**Q.18** Calculate the  $\text{pH}$  of an aqueous solution of 1.0 M ammonium formate assuming complete dissociation ( $\text{pK}_a$  of formic acid = 3.8 and  $\text{pK}_b$  of ammonia = 4.8)

**Sol.**  $\text{HCOONH}_4 + \text{H}_2\text{O} \rightleftharpoons \text{HCOOH} + \text{NH}_4\text{OH}$

The  $\text{pH}$  of the salt of (weak acid and weak base) is given by

$$\text{pH} = \frac{1}{2} [\text{pK}_w + \text{pK}_a - \text{pK}_b] \Rightarrow \text{pH} = \frac{1}{2} [14 + 3.8 - 4.8] = 6.5$$

**Q.19** When 0.100 moles of  $\text{NH}_3$  are dissolved in sufficient water to make 1.00 L of solution, the solution is found to have a hydroxide ion concentration of  $1.33 \times 10^{-3} \text{ M}$ .

(a) What is the  $\text{pH}$  of this solution?

(b) What will be the  $\text{pH}$  of the solution when 0.100 mole of  $\text{NaOH}$  is added to it? Assume no change in volume.

(c) Calculate  $K_b$  for ammonia.

(d) How does  $\text{NaOH}$  added to the solution affect the dissociation of ammonia?

**Sol.** (a)  $[\text{OH}^-] = 1.33 \times 10^{-3} \text{ M}$   $\therefore [\text{H}^+] = \frac{1.00 \times 10^{-14}}{1.33 \times 10^{-3}} = 7.52 \times 10^{-12}$  and  $\text{pH} = 11.12$



(b) When 0.1 mole of NaOH is added, it will completely ionise to give 0.1 mole of  $\text{OH}^-$ . Hydroxyl ions obtained from  $\text{NH}_3$  are negligible in comparison to those obtained from NaOH. Therefore  $[\text{OH}^-] = 10^{-1} \text{ M}$  or  $[\text{H}^+] = 10^{-13} \text{ M}$  or  $\text{pH} = 13$

$$(c) K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{(1.33 \times 10^{-3})^2}{(0.100 - 0.00133)} \quad \text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^- = 1.79 \times 10^{-5}$$

(d) In the presence of NaOH, the ionisation of ammonia is suppressed.

**Q.20** The  $\text{pK}_b$  of  $\text{NH}_4\text{OH}$  is 4.75. An aqueous solution of  $\text{NH}_4\text{OH}$  is titrated with HCl. The pH of the solution at a point when half of  $\text{NH}_4\text{OH}$  is neutralised is

**Sol.** When half of  $\text{NH}_4\text{OH}$  is neutralised

$[\text{NH}_4\text{OH}] = [\text{NH}_4\text{Cl}]$ . By using the Henderson equation,

$$\text{pOH} = \text{pK}_b + \log \frac{[\text{Salt}]}{[\text{Base}]} \quad \text{or } \text{pOH} = 4.75$$

$$\text{pH} = 14 - 4.75 = 9.25$$

**Q.21** Calculate the pH at the equivalent point of the titration between 0.1 M  $\text{CH}_3\text{COOH}$  (25 ml) with 0.05 M NaOH.  $K_a (\text{CH}_3\text{COOH}) = 1.8 \times 10^{-5}$ .

**Sol.** We have already seen that even though when  $\text{CH}_3\text{COOH}$  is titrated with NaOH the reaction does not go to completion but instead reaches equilibrium. We can assume that the reaction is complete and then salt gets hydrolysed because, this assumption will help us to do the problem easily and it does not effect our answer.

$$\therefore [\text{H}^+] = \sqrt{\frac{K_w K_a}{C}}$$

First of all we would calculate the concentration of the salt,  $\text{CH}_3\text{COONa}$ . For reaching equivalence point,

$$\begin{aligned} N_1 V_1 &= N_2 V_2 \\ \therefore 0.1 \times 25 &= 0.05 \times V_2 \\ \Rightarrow V_2 &= 50 \text{ ml} \end{aligned}$$

$$\text{Therefore } [\text{CH}_3\text{COONa}] = \frac{0.1 \times 25}{75} = \frac{0.1}{3}$$

$$\therefore [\text{H}^+] = \sqrt{\frac{10^{-14} \times 1.8 \times 10^{-5}}{0.1/3}} = 2.32 \times 10^{-5} \Rightarrow \text{pH} = -\log 2.32 \times 10^{-5} = 8.63$$

**Q.22** Should  $\text{Mg}(\text{OH})_2$  precipitate from a solution that is 0.01 M  $\text{MgCl}_2$  if the solution is also made 0.10 M in  $\text{NH}_3$ .  $[K_{sp}(\text{Mg}(\text{OH})_2) = 1.8 \times 10^{-11}, K_b(\text{NH}_4\text{OH}) = 1.8 \times 10^{-5}]$

**Sol.**  $[\text{OH}^-]$  in 0.10 M  $\text{NH}_4\text{OH} = \sqrt{K_b C}$ , (Ostwald's dilution law)

$$= \sqrt{1.8 \times 10^{-5} \times 0.10} = 1.34 \times 10^{-3} \text{ M} \quad \Rightarrow [\text{Mg}^{2+}] = 0.01 \text{ M}$$

$$\text{Ionic product} = [\text{Mg}^{2+}][\text{OH}^-]^2 = (0.01) \times (1.34 \times 10^{-3})^2 = 1.8 \times 10^{-8} > K_{sp}$$

Ionic product is greater than  $K_{sp}$  of  $\text{Mg}(\text{OH})_2$  hence precipitation should occur.

**Q.23** The solubility of  $\text{Pb}(\text{OH})_2$  in water is  $6.7 \times 10^{-6}$  M. Calculate the solubility of  $\text{Pb}(\text{OH})_2$  in buffer solution of pH = 8.

**Sol.**  $K_{\text{spPb}(\text{OH})_2} = 4S^3 = 4 \times (6.7 \times 10^{-6})^3$   
 $= 1.203 \times 10^{-15}$

The p of buffer solution = 8, pOH = 6

$$\therefore [\text{OH}^-] = 10^{-6}$$

for left solubility of  $\text{Pb}(\text{OH})_2$

$$[\text{Pb}^{2+}][\text{OH}^-]^2 = K_{\text{sp}}$$

$$\Rightarrow (s)(2s + 10^{-6})^2 = 1.203 \times 10^{-15}$$

$$\Rightarrow s = \frac{1.203 \times 10^{-15}}{10^{-12}} \quad (2s + 10^{-6} \approx 10^{-6})$$

$$\Rightarrow s = 1.203 \times 10^{-3} \text{ mol/lit}$$

**Q.24** Given the solubility product of  $\text{Pb}_3(\text{PO}_4)_2$  is  $1.5 \times 10^{-32}$ . Determine the solubility in gms/litre

**Sol.** Solubility product of  $\text{Pb}_3(\text{PO}_4)_2 = 1.5 \times 10^{-32}$



If x is the solubility of  $\text{Pb}_3(\text{PO}_4)_2$

$$\text{Then } K_{\text{sp}} = (3x)^3(2x)^2 = 108x^5$$

$$x = \sqrt[5]{\frac{K_{\text{sp}}}{108}} = \left( \frac{1.5 \times 10^{-32}}{108} \right)^{\frac{1}{5}}$$

$$x = 1.692 \times 10^{-7} \text{ moles/lit}$$

$$\text{Molecular mass of } \text{Pb}_3(\text{PO}_4)_2 = 811$$

$$x = 1.692 \times 10^{-7} \times 811 \text{ g/lit} = 1.37 \times 10^{-4} \text{ g/lit}$$

Solubility product is

$$K_{\text{sp}}(\text{SrC}_2\text{O}_4) = [\text{Sr}^{2+}][\text{C}_2\text{O}_4^{2-}] = (5.4 \times 10^{-4})^2 = 2.92 \times 10^{-7}$$

**Q.25** Calculate the pH at which an acid indicator with  $K_a = 1 \times 10^{-5}$  changes colour when indicator concentration is  $1 \times 10^{-3}$  M. Also report the pH at which coloured ions is 80% present.

**Sol.** For indicator dissociation equilibrium



Colour A                      Colour B

$$K_{\text{in}} = \frac{[\text{H}^+][\text{In}^-]}{[\text{HIn}]}$$

The mid point of the colour change of an indicator  $\text{HI}_n$  is the point at which  $[\text{In}^-] = [\text{HI}_n]$ ,  $K_{\text{in}} = [\text{H}^+]$

$$= 1 \times 10^{-5}$$

$$\therefore \text{pH} = 5$$

Thus at pH = 5 the indicator will change its colour

$$K_{\text{ind}} = \frac{[\text{H}^+][\text{In}^-]}{[\text{HI}_n]} \quad \Rightarrow 1 \times 10^{-5} = \frac{[\text{H}^+] \times 80/100}{20/100}$$

$$\therefore [\text{H}^+] = 0.25 \times 10^{-5}$$

$$\therefore \text{H} = 5.6020$$

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## s-BLOCK

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The elements in which the last electron enters the outermost s-orbital are called s - block elements. The group 1 and 2 of periodic table belong to the s-block.

### ALKALI METALS

#### ALKALI METAL AND THEIR COMPOUNDS

- (i) **The Elements :** are Li, Na, K, Rb, Cs, Fr (Radioactive :  $t_{1/2}$  of  $\text{Fr}^{233} = 21$  minutes)  
group - I elements are called alkali metals because they form hydroxides on reaction with water, which are alkaline in nature.

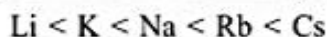
**Outer Electronic configuration :**  $ns^1$

- (ii) **Atomic Radii.** The atomic radii of alkali metals are largest in their respective periods. The atomic radii increase on moving down the group from top to bottom.



- (iii) **Ionic Radii.** Alkali metals change into positively charged ions by losing their outermost electron. These ions are considerably smaller than the parent atoms. Ionic radii increase on moving down the group.

- (iv) **Density.** Alkali metals have low densities due to their large atomic size. Densities increase on going down the group from top to bottom. Potassium is, however lighter than sodium.



**Exception :** Density of  $\text{K} < \text{Na}$  due to abnormal increment in size of K.

- (v) **Ionization Energy.** The first ionization energies of alkali metals are very low as compared with the other elements of the same period.

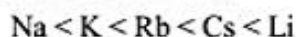


- (vi) **Electropositive Character.** On account of their low ionization energies, these metals have a strong tendency to lose their valence electrons and thus change into positive ions. Consequently, **alkali metals are strongly electropositive or metallic in character.** As this tendency for losing electrons increases down the group, the electropositive character increases.



- (vii) **Oxidation State.** Alkali metals exhibit an oxidation state of +1.

- (viii) **Reducing Character :** All the alkali metals are good reducing agents due to their low ionization energies. Their reducing character, however, follows the order :





The reducing character of any metal is best measured in terms of its electrode potential which among other things depends upon its (i) heat of vaporization (ii) ionization energy and (iii) heat of hydration. Since  $\text{Li}^+$  ion has the smaller size, its heat of hydration has the highest value. Therefore, among the alkali metals Li has the highest negative electrode potential ( $E_{\text{Li}^+/\text{Li}}^0 = -3.05$  volts) and hence is the strongest reducing agent.

Element	Li	Na	K	Rb	Cs	Fr
$E_{\text{M}^+/\text{M}}^0$ (V) at 298 K for	-3.05	-2.71	-2.93	-2.93	-2.92	-
$\text{M}^+(\text{aq.}) + \text{e}^- \rightarrow$	$\text{M}(\text{s})$					

- (ix) **Melting and Boiling point.** The generally low values for cohesive energy are reflected in the very low values of melting and boiling points in the group. The cohesive energy decreases down the group, and the melting points decreases correspondingly.

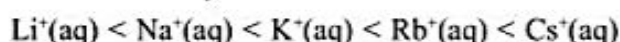
	Melting point ( $^{\circ}\text{C}$ )	Boiling point ( $^{\circ}\text{C}$ )
Li	181	1347
Na	98	881
K	63	766
Rb	39	688
Cs	28.5	705

- (x) **Softness:** These metals are soft and Malleable and have metallic lusture when they are freshly cut due to oscillation of loosely binded electrons.

- (xi) **Ionic Mobility:** 
$$\text{Ionic mobility} \propto \frac{1}{\text{Size of hydrated ion}}$$

Size of the hydrated ion is =  $\text{Li}^+(\text{aq}) > \text{Na}^+(\text{aq}) > \text{K}^+(\text{aq}) > \text{Rb}^+(\text{aq}) > \text{Cs}^+(\text{aq})$

**Order of ionic mobility**



- (xii) **Crystal Structure :** All the Alkali metals have their body centre cubic (BCC) structure with coordination Number 8.

- (xiii) **Flame Colouration.** Alkali metals impart characteristic colours to the flame when they are heated in a Bunsen burner flame.

Li-Carmine Red, Na-Golden Yellow, K- violet (Lilac), Rb-Reddish Violet; Cs-Blue violet

- (xiv) **Colour -** The compounds of alkali metals are typically white

- (xv) **Magnetic behaviour -** The compounds of alkali metals are diamagnetic. Superoxides of alkali metals are, however, paramagnetic.

- (xvi) **Hydration.** Most of alkali metal salts dissolve in water. In solution alkali metal ions are hydrated. Since  $\text{Li}^+$  ion is smallest in size it is most heavily hydrated. Salts of lithium such as  $\text{LiF}$ ,  $\text{Li}_2\text{CO}_3$ ,  $\text{Li}_3\text{PO}_4$  are insoluble in water.



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**Illustration**

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1. The first three elements of Group 1 have the following atomic structures

- (a) Lithium : 3p, 4n; 2, 1 electrons
- (b) Sodium : 11p, 12n; 2, 8, 1 electrons
- (c) Potassium : 19p, 20n; 2, 8, 8, 1 electrons

Which of the following features causes them to have similar properties ?

- (A) The same number of protons
- (B) More protons than electrons
- (C) Two electrons in the first shell
- (D) One electron in the outermost shell.

**Ans.** (D)

**Sol.** One electron in the outermost shell.

2. Considering greater polarization in LiCl compared to that in NaCl, which of the following statements you would expect to be wrong ?

- (A) LiCl has lower melting point than that of NaCl
- (B) LiCl dissolves more in organic solvents
- (C) LiCl will ionize in water more than NaCl
- (D) Fused LiCl would be less conducting than fused NaCl.

**Ans.** (C)

**Sol.** According to Fajan's rules, higher the polarization, higher is the covalent character. Thus, LiCl is covalent while NaCl is ionic. As a result, LiCl will not ionize in water more than NaCl.

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**Exercise**

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1. Sodium ordinarily does not show an oxidation state of +2, because of its

- (A) High first ionization potential
- (B) High second ionization potential
- (C) Large ionic radius
- (D) High electronegativity

**Ans.** (B)

2. Mark the false statement ?

- (A) The electropositive character of alkali metals decreases with increase in atomic number
- (B) Lithium is a hard metal and cannot be cut with a knife
- (C) Alkali metals are strong reducing agents
- (D) Electronegativities of all alkali metals lie between 1.0 to 0.7.

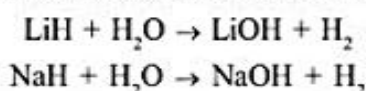
**Ans.** (A)

## CHEMICAL PROPERTIES

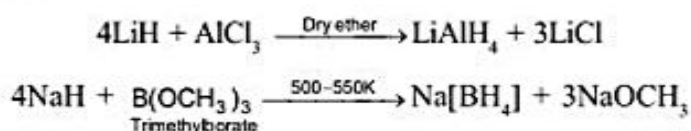
- The alkali metals are highly reactive elements. The reactivity of alkali metals is due to low value of ionization energy; and low heat of atomisation.
- The reactivity of alkali metals increases from Li to Cs
- (i) **Reaction with hydrogen.** Alkali metals react with dry hydrogen to form hydrides.



- These hydrides are ionic in nature and exist as crystalline solids.
- The hydrides of alkali metals react with water to form corresponding hydroxides and hydrogen gas



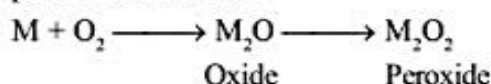
- These hydrides are **strong reducing agents** and their reducing nature **increases down the group**.
- Alkali metals also form complex hydrides such as  $LiAlH_4$  and  $NaBH_4$ , which are also good reducing agents. Alkali metal hydrides do not exist in water and this reaction with any other reagent is carried out in protic solvent.



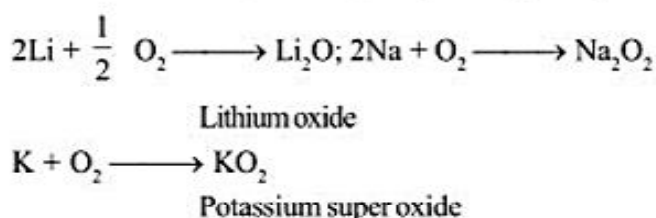
- Fused alkali metal hydrides on electrolysis produce  $H_2$  gas at anode

### (ii) Formation of oxides and hydroxides :

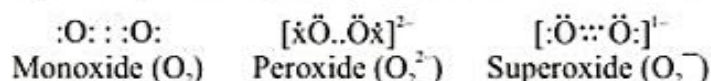
- (a) These are most reactive metals and have strong affinity for  $O_2$ , quickly tarnish in air due to the formation of a film of their oxides on the surface. These are, therefore, kept under kerosene or paraffin oil to protect them from air.



- (b) When burnt in air ( $O_2$ ), lithium forms lithium oxide ( $Li_2O$ ) sodium forms sodium peroxide ( $Na_2O_2$ ) and other alkali metals form super oxide ( $MO_2$  i.e.  $KO_2$ ,  $RbO_2$  or  $CsO_2$ )

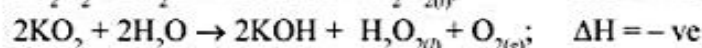
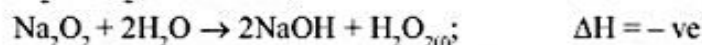
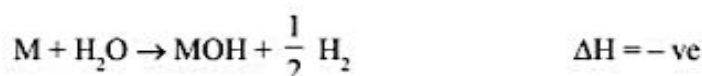


The reactivity of alkali metals towards oxygen to form different oxides is due to strong positive field and thus combines with small anion  $O^{2-}$  to form stable  $Li_2O$  compound. The  $Na^+$  and  $K^+$  being relatively larger thus exert less strong positive field around them and thus reacts with larger oxygen anion i.e.,  $O_2^{2-}$  and  $O_2^{1-}$  to form stable oxides. The monoxide, peroxides and superoxides have  $O_2$  and  $O_2^{2-}$  and  $O_2^{1-}$  ions respectively. The structures of each are,

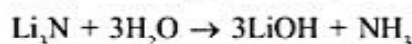
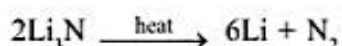


The  $O_2^-$  ion has one three electron covalent bond and has one electron unpaired. It is therefore superoxides are paramagnetic and coloured.  $KO_2$  is light yellow and paramagnetic substance.

The oxides of alkali metals and metal itself give strongly alkaline solution in water with evolution of heat



- (iii) **Reaction with nitrogen.** Lithium is the only element in the group that reacts with dinitrogen to form a nitride. Lithium nitride,  $Li_3N$ , is ionic ( $3Li^+$  and  $N^{3-}$ ), and is ruby red. Two reactions of the nitride are of interest. First, on heating to a high temperature it decomposes to the elements, and second, it reacts with water, giving ammonia.



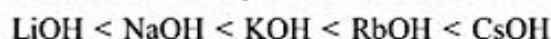
- (iv) **Reaction with water.** The hydroxides of alkali metals are strong bases, all of which are highly soluble in water as well as in alcohol and are stable towards heat. Lithium hydroxide, however, is an exception. It is slightly soluble in water and loses a water molecule on heating.



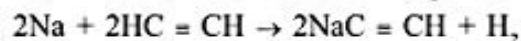
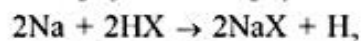
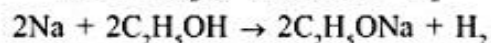
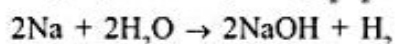
The basic character of alkali metal hydroxides increases in going down the group. This can be explained in terms of decreasing polarising power of alkali metal ions.

$LiOH$  is relatively covalent. As moving down the group ionic nature of hydroxides increases. More the ionic nature of hydroxide; basic nature of hydroxide will increase.

Thus, the basic character of alkali metal hydroxides is in the order:



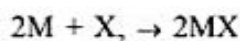
- (v) **Reaction with Water.** Alkali metals react with water and other compounds containing acidic hydrogen atoms such as hydrogen halides ( $HX$ ) and acetylene ( $C_2H_2$ ) and liberate hydrogen gas.



On descending the group from lithium to caesium, the vigour of the reaction increases.

All the alkali metals when exposed to atmosphere react with oxygen and moisture to form oxides and hydroxides and therefore their surface gets tarnished. In order to protect from atmospheric oxygen and water, these metals are stored under kerosene oil.

- (vi) **Reaction with Halogens** - Alkali metals react with halogens to form metal halides, which are ionic crystalline solids having general formula  $M^+X^-$ .



All the halides of alkali metals except lithium fluoride are freely soluble in water. The low solubility of lithium fluoride is attributed to greater force of attraction between lithium ions and fluoride ions in the crystal lattice.



- (vii) **Reaction with Non Metals** - Alkali metals, on heating react with non – metals such as sulphur and phosphorus to form sulphides and phosphides respectively.

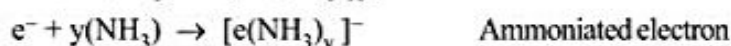
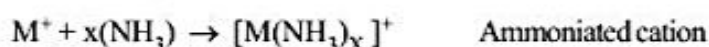
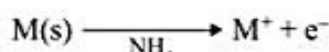


- (viii) **Solubility in Liquid Ammonia.**

Alkali metals dissolve in liquid ammonia (high conc. 5 M) and give blue solution which is conducting, reducing and paramagnetic in nature.

**Reason**

On dissolving Metal in  $NH_3$

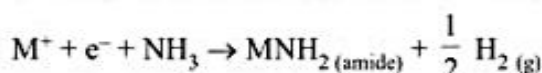


The blue colour is due to  $\rightarrow$  Ammoniated electron

The paramagnetic nature is due to  $\rightarrow$  Ammoniated electron

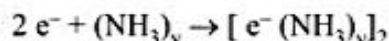
The conducting nature is due to  $\rightarrow$  Ammoniated  $M^+$  + Ammoniated electron

- \* On standing the colour fades due to formation of amide



In the absence of impurities like Fe, Pt, Zn etc, the solutions are stable.

- \* In concentrated solution, the blue colour changes to bronze colour and diamagnetic due to the formation of metal clusters and ammoniated electrons also associate to form electron pairs



- (ix) **Complex Compounds.** The alkali metal ions form fewer complex compounds than any other group of metal ions. This is due to their large atomic size and weak effective nuclear charge. The complex forming ability decreases in the order :



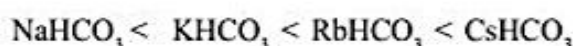
- (x) **Nature of carbonate and Bicarbonate salts:** Except  $Li_2CO_3$ , other metal carbonates do not decompose even at high temperature due to their high ionic character.

Order of Solubility in water :  $Li_2CO_3 < Na_2CO_3 < K_2CO_3 < Rb_2CO_3 < Cs_2CO_3$

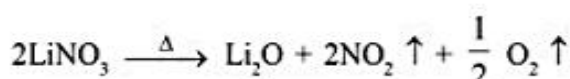
Except  $LiHCO_3$ , all the alkali metal bicarbonate exist.

$NaHCO_3$  exist in polymeric form and  $KHCO_3$  exist in dimeric form due to the presence of intermolecular hydrogen bonding.

Order of solubility



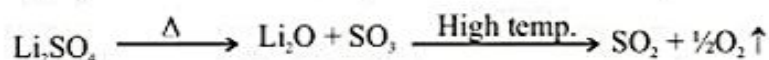
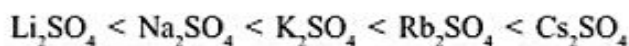
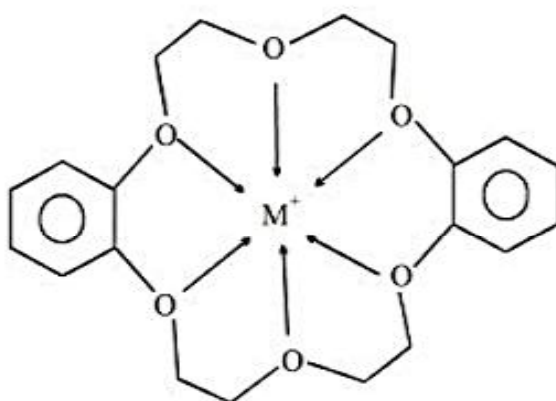
- (xi) **Nature of Nitrate Salt:**



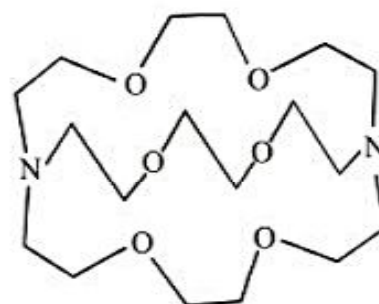


**(xii) Nature of sulphate Salts:**

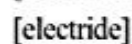
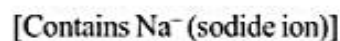
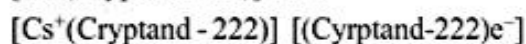
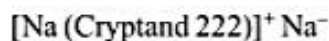
Except  $\text{Li}_2\text{SO}_4$  other alkali metal sulphate salts do not decompose even at high temperature

**Order of solubility:****(xiii) Crown Ethers and Cryptands:**

Dibenzo-18-Crown-6



Cryptand - 222

**DIAGONAL RELATIONSHIP**

Lithium shows diagonal relationship with magnesium since they have almost the same polarizing power, i.e., charge/size ratio.

Lithium resembles magnesium in the following respects :

- (i) atomic size of Li (1.34 Å) and Mg (1.36 Å) are not much different.
- (ii) ionic size of  $\text{Li}^+$  (0.60 Å) and  $\text{Mg}^{2+}$  (0.65 Å) are almost identical.
- (iii) polarizing power (i.e., ionic charge to ionic radius ratio) of  $\text{Li}^+$  and  $\text{Mg}^{2+}$  are about the same
- (iv) electronegativities of Li (1.00) and Mg (1.20) are not much different
- (v) both Li and Mg are hard metals
- (vi) both decompose water only on heating
- (vii) both combine with oxygen to form monoxides,
- (viii) both  $\text{LiOH}$  and  $\text{Mg}(\text{OH})_2$  are weak bases
- (ix) both  $\text{LiCl}$  and  $\text{MgCl}_2$  are predominantly covalent and hence are soluble in organic solvents, such as alcohol and pyridine
- (x) both Li and Mg combine with nitrogen to form their respective nitrides,  $\text{Li}_3\text{N}$  and  $\text{Mg}_3\text{N}_2$

- (xi) carbonates, fluorides, oxalates and phosphates of both Li and Mg are sparingly soluble in  $H_2O$
- (xii) the hydroxides and carbonates of both Li and Mg decompose on heating forming their respective oxides
- (xiii) both lithium and magnesium nitrates on heating evolve  $NO_2$  and  $O_2$  leaving behind their oxides.

## ORES OF ALKALI METALS

Since alkali metals are highly reactive metals, they do not occur in free state in nature. *Sodium and potassium are quite abundant in the earth's crust with 7<sup>th</sup> and 8<sup>th</sup> position in the order of abundance of elements.*

### (A) Ores of Lithium

- (i) Spodumene,  $LiAlSi_2O_6$
- (ii) Lepidolite,  $(Li)_2 Al_2(SiO_3)_3 \cdot (FOH)_2$

### (B) Ores of Sodium

- (i) Common salt or rock salt,  $NaCl$
- (ii) Chile salt patre,  $NaNO_3$
- (iii) Albite (Soda Feldspar),  $NaAlSi_3O_8$
- (iv) Glauber's salt,  $Na_2SO_4 \cdot 10H_2O$
- (v) Borax,  $Na_2B_4O_7 \cdot 10H_2O$

### (C) Ores of Potassium

- (i) Carnallite,  $KCl \cdot MgCl_2 \cdot 6H_2O$
- (ii) Feldspar,  $KAlSi_3O_8$
- (iii) Sylvine,  $KCl$

## EXTRACTION OF ALKALI METALS

### (i) Lithium : Extraction of lithium involves two steps

1. Preparation of  $LiCl$  from the ore
2. Electrolysis of  $LiCl$

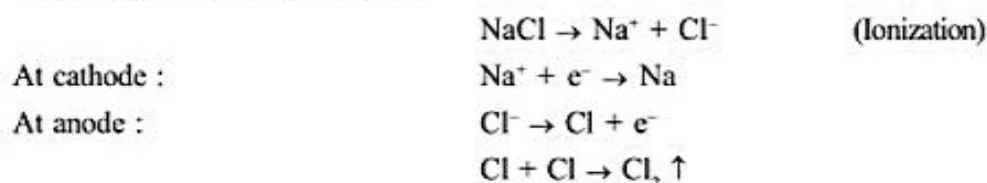
During electrolysis the electrolyte used is 55%  $LiCl$  and 45%  $KCl$ . The electrolyte is maintained in molten state by heating to about 723 K.

### (ii) Sodium :

#### Down's Process

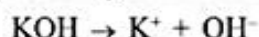
In this method, sodium is obtained by the electrolysis of a mixture of sodium chloride (40%) and calcium chloride (60%) in fused state. The function of calcium chloride is to lower the operating temperature from 1080 K (m.pt. of  $NaCl$ ) to about 850 K.

The following reactions take place:



The sodium metal obtained by this method is about 99% pure. *Chlorine is the by – product in this process.*

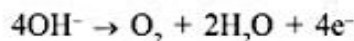
(iii) **Potassium** : Potassium is obtained by electrolysis of fused potassium hydroxide (KOH)



At cathode :



At anode :



### Illustration

1. Alkali metals readily dissolve in liquid ammonia to give blue coloured solutions. The blue colour is believed to be due to

(A) Ammoniated cations

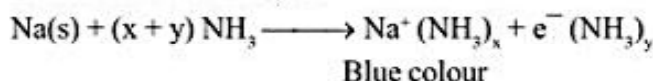
(B) Ammoniated anions

(C) Ammoniated electrons

(D) Ammoniated cations and ammoniated electrons

Ans. (C)

Sol. Ammoniated electrons, i.e.



2. Choose the compound which does not possess a peroxide group

(A)  $\text{Na}_2\text{O}_2$

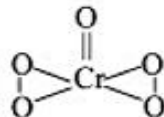
(B)  $\text{CrO}_5$

(C)  $\text{Fe}_2\text{O}_3$

(D)  $\text{BaO}_2$

Ans. (C)

Sol.  $\text{Na}_2\text{O}_2$  is  $\text{Na}^+ \text{O}^- \text{O}^- \text{Na}^+$ ;  $\text{CrO}_5$  is



$\text{BaO}_2$  is  $\text{Ba}^{2+} (\text{O}^- \text{O}^-)$  while  $\text{Fe}_2\text{O}_3$  consists of only  $\text{Fe}^{3+}$  and  $\text{O}^{2-}$  ions. Thus,  $\text{Fe}_2\text{O}_3$  does not contain a peroxide  $[\text{O}^- \text{O}^-]$  linkage.

### Exercise

1. The addition of  $\text{Na}_2\text{CO}_3$  to the aqueous solution of an oxide produces  $\text{CO}_2$ . This reaction indicates that

(A) Oxide is basic

(B) Oxide is amphoteric

(C) Oxide is that of a metal

(D) Oxide is that of a non-metal

Ans. (D)

2. Alkali metals when exposed to air tarnish quickly due to the

(A) Formation of their hydroxides

(B) Formation of their carbonates

(C) Formation of their oxides

(D) All the above

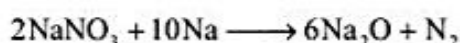
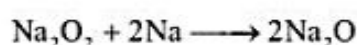
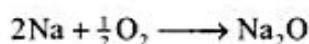
Ans. (D)

## COMPOUND OF ALKALI METALS

### SODIUM

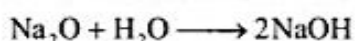
#### (1) Sodium Monoxide ( $\text{Na}_2\text{O}$ )

**Preparation:** It is obtained by burning sodium at  $180^\circ\text{C}$  in a limited supply of air or oxygen and distilling off the excess of Na in vacuum or by heating  $\text{Na}_2\text{O}_2$  (sodium peroxide), sodium nitrate ( $\text{NaNO}_3$ ) with sodium.

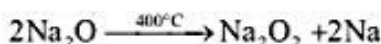


**Properties:**

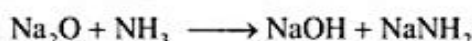
- (i) It is a white amorphous substance.
- (ii) It reacts with water violently forming NaOH.



- (iii) On heating above  $400^\circ\text{C}$ , it disproportionate to give peroxide and metallic sodium.



- (iv) It reacts with liquid ammonia forming sodamide and NaOH.



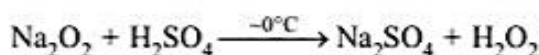
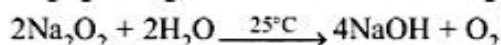
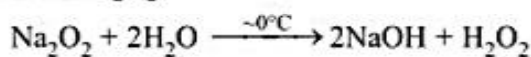
#### (2) Sodium Peroxide ( $\text{Na}_2\text{O}_2$ )

**Preparation:** It is formed by heating the metal in excess of air or oxygen at  $300^\circ$ , which is free from moisture and  $\text{CO}_2$ .

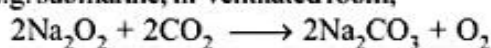


**Properties:**

- (i) It is a pale yellow solid, becoming white in air from the formation of a film of NaOH and  $\text{Na}_2\text{CO}_3$ .
- (ii) In cold water ( $\sim 0^\circ\text{C}$ ) produces  $\text{H}_2\text{O}_2$  but at room temperature produces  $\text{O}_2$ . In ice-cold mineral acids also produces  $\text{H}_2\text{O}_2$ .

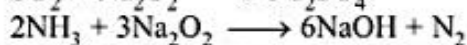
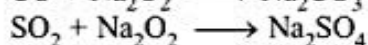
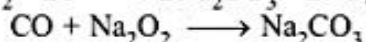


- (iii) It reacts with  $\text{CO}_2$ , giving sodium carbonate and oxygen and hence its use for purifying air in a confined space e.g. submarine, ill-ventilated room,





- (iv) It is an oxidising agent and oxidises charcoal, CO, NH<sub>3</sub>, SO<sub>2</sub>.  
 $3\text{Na}_2\text{O}_2 + 2\text{C} \longrightarrow 2\text{Na}_2\text{CO}_3 + 2\text{Na}$  [deposition of metallic Na]



- (v) It contains peroxide ion  $[\text{O}-\text{O}]^{2-}$

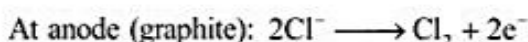
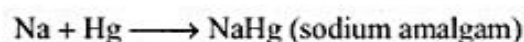
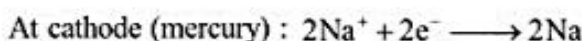
#### Uses:

- For preparing H<sub>2</sub>O<sub>2</sub>, O<sub>2</sub>
- Oxygenating the air in submarines
- Oxidising agent in the laboratory.

### (3) Sodium Hydroxide (Caustic Soda), NaOH

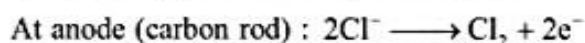
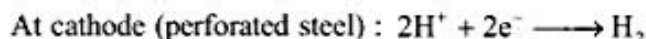
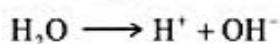
**Preparation:** Sodium hydroxide is commonly called caustic soda therefore used for air purify and it is prepared by electrolytic process. There are two electrolytic methods commonly used for preparing sodium hydroxide.

#### (a) Castner Kellner cell:



Sodium amalgam is removed from the cell. It is then decomposed in a separate cell by water giving NaOH, hydrogen and mercury. Mercury is recirculated to the cell.

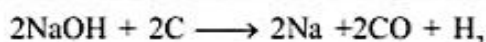
#### (b) Nelson cell (or Diaphragm cell)



**Note:** This cell is used for the industrial production of Cl<sub>2</sub>. As well as this cell can be used for production of Na<sub>2</sub>CO<sub>3</sub>, for which CO<sub>2</sub> is mixed with steam.

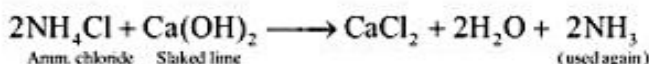
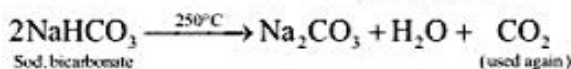
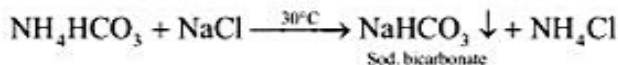
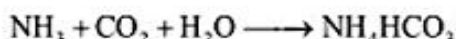
#### Properties:

NaOH is stable towards heat but is reduced to metal when heated with carbon



- (4) **Sodium Carbonate (Na<sub>2</sub>CO<sub>3</sub>) :** It exists in various forms, namely anhydrous sodium carbonate Na<sub>2</sub>CO<sub>3</sub> (soda-ash); monohydrate, Na<sub>2</sub>CO<sub>3</sub>·H<sub>2</sub>O (crystal carbonate); heptahydrate, Na<sub>2</sub>CO<sub>3</sub>·7H<sub>2</sub>O and decahydrate, Na<sub>2</sub>CO<sub>3</sub>·10H<sub>2</sub>O (washing soda). It occurs in the form of reh and sajji matti in U.P. and Bihar.

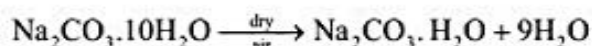
**Manufacture: (Solvay or ammonia soda process).** In this process, brine (NaCl), ammonia and carbon dioxide are the raw materials. The chemical reactions involved are as below.



**Note:** Solvay process can not be used for the production of  $\text{K}_2\text{CO}_3$ , since  $\text{KHCO}_3$  has much greater solubility than  $\text{NaHCO}_3$ . So,  $\text{KHCO}_3$  cannot be precipitated.

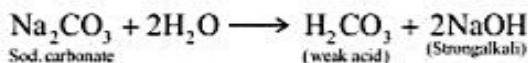
**Properties:**

- (i) Sodium carbonate crystallizes from water as decahydrate. It is a white solid which efflorescence on exposure to dry air forming the monohydrate.

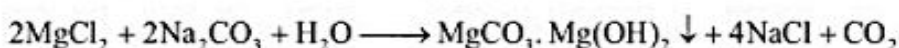


On heating, the monohydrate changes to anhydrous salt (m.p.  $853^\circ\text{C}$ ) which does not decompose on further heating even to redness.

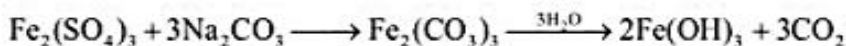
- (ii) It is soluble in water with considerable evolution of heat. The resulting solution is alkaline due to hydrolysis.



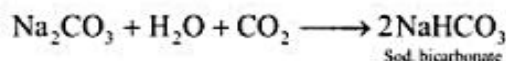
- (iii) It is readily decomposed by acids with the evolution of  $\text{CO}_2$  gas.  
(iv) It reacts with metal salts to form insoluble normal or basic carbonate.



Carbonates of metals like Al, Fe, Sn, etc. When formed are immediately hydrolysed to hydroxides.



- (v) When  $\text{CO}_2$  gas is passed through aqueous solution of sodium carbonate, sodium bicarbonate is formed.



- (5) **Sodium Sulphate ( $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$ ) (Glauber's salt)**

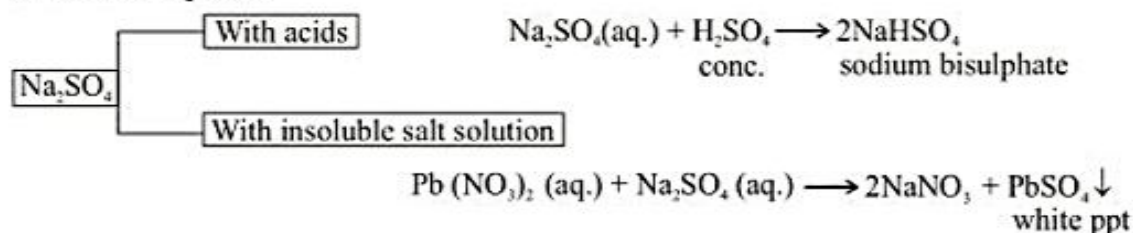
**Preparation** - By heating a mixture of common salt & conc.  $\text{H}_2\text{SO}_4$  (Le blanc process)



**Properties**

**Physical properties :**

- (i) Crystalline solid, which is soluble in water.  
(ii) Crystallizes as decahydrate & on heating becomes anhydrous.

**Chemical Properties****(6) Sodium Chloride (NaCl)****Preparation:**

It is also called common salt occurs abundantly in nature as rock salt or halite. The most abundant source is sea-water where sodium chloride occurs to the extent of 2.6 – 2.9 percent. The sea water is exposed to the sun and air in large shallow pits. The gradual evaporation of water lead to the crystallization of the salt. The purification is done by dissolving the salt in minimum volume of water and filtering, if necessary, to remove insoluble impurities. The solution is then saturated with a current of dry hydrogen chloride whereby crystals of pure sodium chloride separate out.

**Properties:**

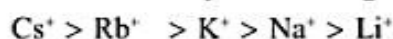
- (i) NaCl is a colourless crystalline salt, almost insoluble in alcohol and highly soluble in water.
- (ii) It gives rise to HCl when heated with conc.  $\text{H}_2\text{SO}_4$  and  $\text{Cl}_2$ , with  $\text{MnO}_2$  plus  $\text{H}_2\text{SO}_4$ .
 
$$\text{NaCl} + \text{H}_2\text{SO}_4 \longrightarrow \text{NaHSO}_4 + \text{HCl} \uparrow$$

$$\text{NaHSO}_4 + \text{NaCl} \longrightarrow \text{Na}_2\text{SO}_4 + \text{HCl} \uparrow$$

$$2\text{NaCl} + \text{MnO}_2 + 2\text{H}_2\text{SO}_4 \longrightarrow \text{MnSO}_4 + \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O} + \text{Cl}_2 \uparrow$$

**Illustration**

Give reason for decreasing order of conductivity of following



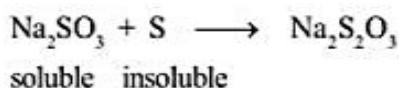
**Sol.** Ions are hydrated in solution. Since Li is very small it is heavily hydrated. This make the radius of the hydrated ions large and hence it moves only slowly (although  $\text{Li}^+$  is very small) and the radius of hydrated  $\text{Cs}^+$  ion is smaller than the radius of hydrated  $\text{Li}^+$ .

**(7) Sodium Thiosulfate ( $\text{Na}_2\text{S}_2\text{O}_3$ )·5H<sub>2</sub>O**

Sodium thiosulfate is a salt of an unstable acid  $\text{H}_2\text{S}_2\text{O}_3$  (thiosulphuric acid)

**Preparation**

- (i) sodium sulfite and flowers of S



- (ii) Spring's Reaction

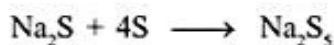
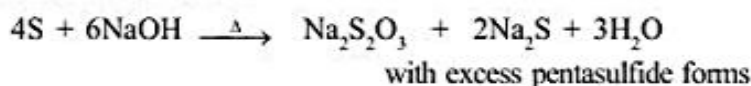


- (iii) sodium carbonate solution with  $\text{SO}_2$



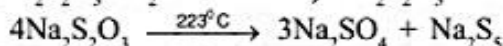


(iv) sulfur and caustic soda

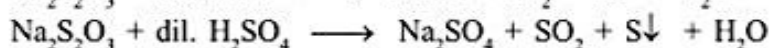
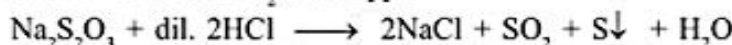


### Chemical Properties

(i) **Heating effect** -  $Na_2S_2O_3 \cdot 5H_2O \xrightarrow{215^\circ C} Na_2S_2O_3 + 5H_2O$



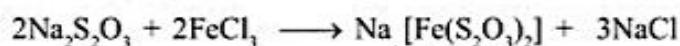
(ii) **Acidification** - liberates  $SO_2$  and S ppt.



(iii) **Reduction** -  $Na_2S_2O_3 + Cl_2 + H_2O \longrightarrow Na_2SO_4 + 2HCl + S$

chlorine

water



↓ (Purple)

FeCl<sub>2</sub> (green)

(iv) **Oxidation** - (oxidises by  $I_2$  quantitatively)



sodium

tetrathionate

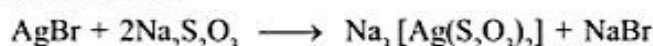
(v) **AgNO<sub>3</sub> action** -  $2AgNO_3 + Na_2S_2O_3 \longrightarrow Ag_2S_2O_3 + 2NaNO_3$



Thus white ppt. of silver thiosulfate changes as

White  $\longrightarrow$  yellow  $\longrightarrow$  brown  $\longrightarrow$  black

(vi) **Silver halide action**



sodium argento

thiosulfate(colourless)

this property is used in photography fixing.

(vii) **Action on CuSO<sub>4</sub>**



cupric

thiosulfate

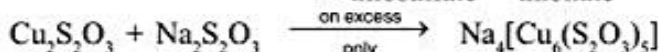


cuprous

thiosulfate

sodium tetra

thionate



sodium cupro thiosulfate(sol)

(8) **Sodium Bicarbonate (NaHCO<sub>3</sub>)**

**Preparation :** Sodium bicarbonate is prepared by the Solvay Process. It is infact formed in between the manufacture of washing soda.



- \* Aqueous solution gives no colour with phenolphthalein but yellow colour with Methyl orange and hence is weakly basic.
- \*  $2\text{NaHCO}_3 \xrightarrow{\Delta} \text{Na}_2\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O}$
- \* Salts which give basic carbonates with washing soda give normal salts with the bicarbonate.  
 $\text{ZnSO}_4 + 2\text{NaHCO}_3 \longrightarrow \text{ZnCO}_3 + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O} + 2\text{CO}_2$
- \* It is used as "SODA BICARB" to neutralise stomach acidity.
- \* Sodium/Potassium salt of tartaric acid and  $\text{NaHCO}_3$  mixture is used as Baking Soda.

### Illustration

1. Based on lattice energy and other considerations which one of the following alkali metal chlorides is expected to have the highest melting point

(A) LiCl (B) NaCl (C) KCl (D) RbCl

Ans. (B)

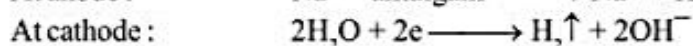
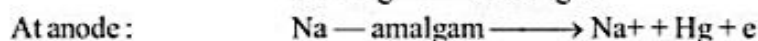
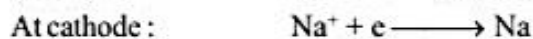
Sol. Although lattice energy of LiCl higher than NaCl but LiCl is covalent in nature and NaCl ionic there, after, the melting point decreases as we move NaCl because the lattice energy decreases as a size of alkali metal atom increases (lattice energy  $\propto$  melting point of alkali metal halide)

2. NaOH is prepared by the method

(A) Down's cell (B) Castner cell (C) Solvay process (D) Castner Kellner cell

Ans. (D)

Sol. The cell involves the following reaction,



### Exercise

1. Sodium thiosulphate ( $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ ) is used in photography to
- (A) Reduce silver bromide to metallic silver  
 (B) Convert metallic silver to silver salt  
 (C) Remove undecomposed AgBr as a soluble silver thiosulphate complex  
 (D) Remove unreduced silver

Ans. (C)

2. Which of the following pair can't exist in solution

(A)  $\text{NaHCO}_3$  and NaOH (B)  $\text{Na}_2\text{CO}_3$  and NaOH  
 (C)  $\text{Na}_2\text{CO}_3$  and NaCl (D)  $\text{NaHCO}_3$  and NaCl

Ans. (A)

## POTASSIUM

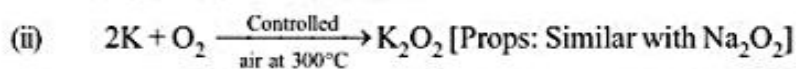
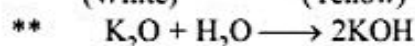
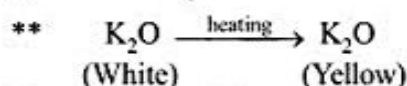
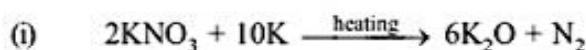
### POTASSIUM AND ITS COMPOUNDS

- Atomic Number : 19
- Electronic Configuration : 2, 8, 8, 1
- Valency and Oxidation state : + 1
- Occurrence :** Potassium is highly reactive metal. It does not occur in nature in free form. Its important minerals are :  
(a) Pearl ash,  $K_2CO_3$  (b) Sylvine, KCl. (c) Indian Salt petre,  $KNO_3$  (d) Camallite,  $KCl \cdot MgCl_2 \cdot 6H_2O$
- Extraction :** It may be prepared by any of the following methods :  
(a) By electrolysis of fused potassium cyanide.  
(b) By heating potassium fluoride with calcium.  
(c) By heating potassium carbonate with carbon (coke).  
(d) By electrolysis of molten KCl containing a little KF.
- Properties :**  
(a) Potassium is a silvery white metal (M.P.  $65^\circ$ ).  
(b) It is lighter and softer than sodium. It resembles sodium in its chemical properties, but is more reactive than it.  
(c) Potassium decomposes cold water more vigorously than sodium. The heat of reaction is so high that the hydrogen gas evolved catches fire. When excess of metal is burnt in air or oxygen under reduced pressure,  $K_2O$  is formed. When heated in excess of air, potassium forms superoxide ( $KO_2$ ).  
(d) Potassium (40) is feebly radioactive. It is a  $\beta$ -emitter. It has 3 isotopes of mass 39, 40 and 41 of which the first one is present in larger proportions. The radioactivity is due to the presence of isotope of mass number 40 which makes up about 0.012% of the metal.
- Uses :**  
(a) Potassium is used in photoelectric cells.  
(b) An alloy of sodium and potassium which is liquid is used in high temperature thermometers.

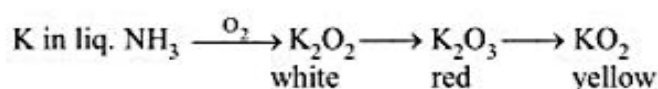
(i) **Oxides of Potassium:**

$K_2O$ ,	$K_2O_2$ ,	$K_2O_3$ ,	$KO_2$	and	$KO_3$
Colours: White	White	Red	Bright Yellow		Orange Solid

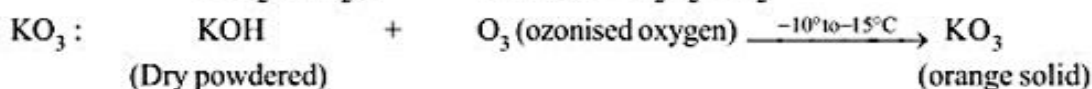
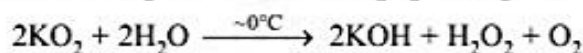
**Preparation:**



(iii) Passage of  $O_2$  through a blue solution of K in liquid  $NH_3$  yields oxides  $K_2O_2$  (white),  $K_2O_3$  (red) and  $KO_2$  (deep yellow) i.e



\*\*  $\text{KO}_2$  reacts with  $\text{H}_2\text{O}$  and produces  $\text{H}_2\text{O}_2$  and  $\text{O}_2$  both



(ii) **Potassium hydroxide (Caustic Potash), KOH**

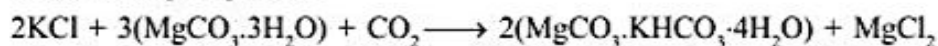
**Preparation:** It may be prepared like that of NaOH, i.e., by the electrolysis of KCl solution and by the action of lime on potassium carbonate. It may also be obtained by the action of baryta,  $\text{Ba(OH)}_2$  on potassium sulphate.



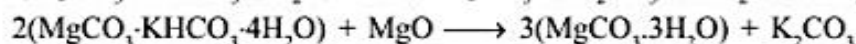
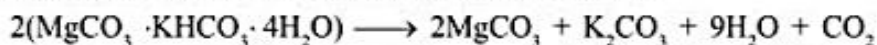
**Properties:** Its properties are similar to those of sodium hydroxide. However, it is a stronger alkali and more soluble in alcohol and is therefore, used in organic reactions instead of caustic soda. Moreover, it is a better absorber of  $\text{CO}_2$  than NaOH because potassium carbonate is more soluble and does not separate out. Its aqueous solution is known as potash lye.

(iii) **Potassium carbonate ( $\text{K}_2\text{CO}_3$ ):** It is also known as pearl ash.

**Preparation:** It is made by passing  $\text{CO}_2$  into a conc. solution of the chloride, containing hydrated magnesium carbonate in suspension at  $20^\circ\text{C}$  when an insoluble potassium hydrogen magnesium carbonate is precipitated.



The precipitate is separated by filtration, and then decomposed either by heating with water under pressure at  $140^\circ\text{C}$  or by the action of magnesium oxide below  $20^\circ\text{C}$ .



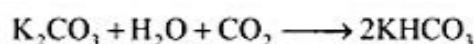
**Properties:**

(i) It is white, deliquescent solid

(ii)  $\text{K}_2\text{CO}_3$  resembles  $\text{Na}_2\text{CO}_3$  in properties, but is more alkaline and more soluble than  $\text{Na}_2\text{CO}_3$ .

(iv) **Potassium Bicarbonate ( $\text{KHCO}_3$ )**

**Preparation:** It is prepared by passing  $\text{CO}_2$  through a cold saturated solution of potassium carbonate.



**Properties:** It resembles sodium bicarbonate in all respects except that it is more soluble in water. It is used in medicine and in baking powders.

(v) **Potassium Sulphate ( $\text{K}_2\text{SO}_4$ )**

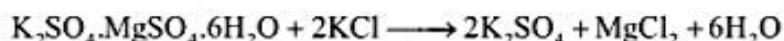
**Preparation:**

(i) By treating KCl or KOH with  $\text{H}_2\text{SO}_4$





- (ii) By treating naturally occurring mineral, schonite ( $K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$ ) with sylvine (KCl).



**Properties:**

- (i) It is a white crystalline (m.p.  $1050^\circ C$ ) solid, not very soluble in water.
- (ii) Unlike sodium sulphate, its crystals do not contain water of crystallisation.
- (iii) When heated with carbon, it is reduced to potassium sulphide.
- (iv) It forms a series of double salts with the sulphates of trivalent metals, e.g. potash alum,  $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ .

**(vi) Potassium Chloride (KCl)**

**Preparation:** KCl is prepared from fused carnallite. Nearly pure KCl separates from the melt, leaving fused  $MgCl_2$  behind.



**Properties:** It is a colourless cubic crystal soluble in water. Its solubility increases almost linearly with temperature.

**Illustration**

1. Which is an ore of potassium

(A) Camallite (B) Cryolite (C) Bauxite (D) Dolomite

**Ans. (A)**

**Sol.** Camallite -  $KCl \cdot MgCl_2 \cdot 6H_2O$

Cryolite -  $Na_3AlF_6$

Bauxite -  $(Al_2O_3 \cdot 2H_2O)$

Dolomite -  $MgCO_3 \cdot CaCO_3$

2. KF combination with HF to form  $KHF_2$ . The compound contains the species

(A)  $K^+$ ,  $F^-$  and  $H^+$  (B)  $K^+$ ,  $F^-$  and HF (C)  $K^+$  and  $[HF_2]^-$  (D)  $[KHF]^+$  and  $F^-$

**Ans. (C)**



**Exercise**

1. When potassium dichromate crystal are heated with conc. HCl

(A)  $O_2$  is evolved (B) Chromyl chloride vapours are evolved  
(C)  $Cl_2$  is evolved (D) No reaction takes place

**Ans. (C)**

2. When potassium ferrocyanide crystals are heated with concentrated sulphuric acid, the gas evolved is

(A) Ammonia (B) Sulphur dioxide (C) Carbon dioxide (D) Carbon monoxide

**Ans. (D)**



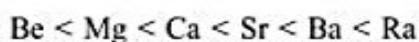
## ALKALINE EARTH METALS

### ALKALI EARTH METAL & THEIR COMPOUNDS

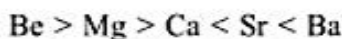
- (a) The group IIA consists of six elements - Be, Mg, Ca, Sr, Ba, Ra.  
Collectively called alkali earth metals.
- (b) Ra was discovered in the ore pitch blende by madam curie, it is radioactive in nature.
- (c) The first member Beryllium is less active than other members and shows abnormal properties like lithium in IA group.

### PHYSICAL PROPERTIES

- (i) **Electronic configuration :** *The Elements* are Be, Mg, Ca, Sr, Ba Ra,  
**Outermost Electronic configuration :** -  $ns^2$
- (ii) **Atomic Radii.** The atomic radii of alkaline earth metals are quite larger but are smaller than those of alkali metals.



- (iii) **Density.** The densities of alkaline earth metals are larger than those of alkali metals. This is due to stronger metallic bond. Density of alkaline earth metals first decreases from Be to Ca and then increases from Ca to Ra.



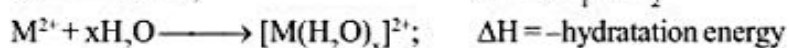
- (iv) **Cohesive Forces.** Cohesive forces in alkaline earth metals are stronger than alkali metals due to smaller atomic radii and greater nuclear charge. Alkaline earth metals are harder than alkali metals due to stronger metallic bond.
- (v) **Melting and Boiling points**  
They have low m.p. and b.p. but are higher than corresponding value of group I.

**Reason :** They have two valency electrons which may participate in metallic bonding compared with only one electron in AM. Consequently group II elements are harder and have higher cohesive energy and  $\therefore$  have much higher m.p./b.p. than A.M.

M.P.  $\text{Be} > \text{Ca} > \text{Sr} > \text{Ba} > \text{Mg}$

B.P.  $\text{Be} > \text{Mg} > \text{Ca} > \text{Ba} > \text{Sr}$

- (vi) **Ionization energy.** The alkaline earth metals owing to their large size of atoms have fairly low values of **ionization energies** as compared to the p block elements. However, within the group, the ionization energy, decreases as the atomic number increases.
- (vii) **Electropositive character.** These are less electropositive than alkali metals.
- (viii) **Oxidation Number :** The tendency of these metals to exist as divalent cation as  $\text{IE}_1$  is much lower than  $\text{IE}_2$ , so they should be form univalent in rather than divalent ion but actually these give bivalent ions.
- (ix) This is due the fact that  $\text{M}^{2+}$  ion possesses a higher degree of hydration or  $\text{M}^{2+}$  ions are extensively hydrated form  $[\text{M}(\text{H}_2\text{O})_x]^{2+}$  a hydrated ion.



- (x) **Reducing properties.** The members of this group are weaker reducing agents than the alkali metals.  

$$\text{Be} < \text{Mg} < \text{Ca} < \text{Sr} < \text{Ba}$$
- (xi) **Flame colouration.** Among the members of this group except Be and Mg all other members give characteristic colouration to the flame. Beryllium and magnesium do not impart any colour to the flame because of their small size and higher ionization energies. Due to this, the energy of flame is insufficient to cause the excitation of their valence electrons to higher shells.  
 Ca – Brick Red, Sr – Crimson Red, Ba – Apple green
- (xii) **Solubility of Liquid Ammonia.** All these metals dissolve in liquid  $\text{NH}_3$ .

### Illustration

1. In alkaline earth metals, the electrons are more firmly held to the nucleus and hence  
 (A) Ionization energy of alkaline earth metals is greater than that of alkali metals  
 (B) Alkaline earths are less abundant in nature  
 (C) Reactivity of alkaline earth metals is greater than that of alkali metals  
 (D) Atoms of alkaline earth metals are bigger in size than alkali metals.

**Ans.** (A)

**Sol.** Ionization energies of alkaline earth metals are greater than those of alkali metals due to increased nuclear charge.

2. The ion having highest mobility in aqueous solution is  
 (A)  $\text{Be}^{2+}$  (B)  $\text{Mg}^{2+}$  (C)  $\text{Ca}^{2+}$  (D)  $\text{Ba}^{2+}$

**Ans.** (D)

**Sol.** Though  $\text{Ba}^{2+}$  is the heaviest ion but it is least hydrated. As a result, its size becomes lesser than any other hydrated alkaline earth metal cation and hence has the highest ionic mobility.

### Exercise

1. Alkaline earth metal show typical characteristics of  
 (A) Inner transition elements (B) Noble gases  
 (C) Representative elements (D) Transition elements

**Ans.** (C)

2. Which of the following is true for magnesium?  
 (A) It is more electropositive than sodium  
 (B) It is manufactured by electrolysis of aqueous magnesium chloride  
 (C) It is a strong reducing agent  
 (D) It resembles, in chemical properties, with its diagonally placed element Boron in 13 group of the Periodic Table.

**Ans.** (C)

## CHEMICAL PROPERTIES

- Alkaline earth metals are **quite reactive** elements due to their low ionization energies and high electropositive character. The reactivity of these elements increases with increase in atomic number.

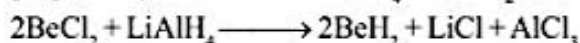
- Alkaline earth metals are less reactive than alkali metals.

(i) **Hydrides :**

- (a) Except Be, all alkaline earth metals form hydrides ( $MH_2$ ) on heating directly with  $H_2$ .



- (b)  $BeH_2$  is prepared by the action of  $LiAlH_4$  on  $BeCl_2$



- (c)  $BeH_2$  and  $MgH_2$  are covalent while other hydrides are ionic.

- (d) The ionic hydrides of Ca, Sr, Ba liberate  $H_2$  at anode and metal at cathode.



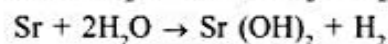
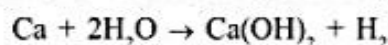
- (e) The stability of hydrides decreases from Be to Ba.

- (f) The hydrides having higher reactivity for water, dissolve readily and produce hydrogen gas.

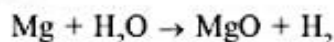
- (g) The hydrides having higher reactivity for water, dissolve readily and produce hydrogen gas.



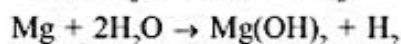
- (ii) **Reaction with water.** Ca, Sr and Ba react with cold water, liberating hydrogen gas



Magnesium decomposes hot water

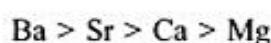


Or

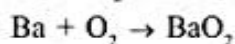
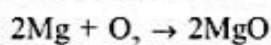


Beryllium does not react with water.

Order of Reactivity :



- (iii) **Reaction with Oxygen.** All the alkaline earth metals burn in oxygen to form oxides. Be, Mg and Ca form oxides whereas Ba and Sr form peroxides.



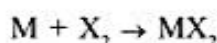
- (iv) **Hydroxides.** The hydroxides of these elements can be formed either by dissolving metal oxides in water or by reaction of these elements with water.

$Be(OH)_2$  is amphoteric. The hydroxides of magnesium, calcium, strontium and barium are bases and their strength increases from magnesium to barium.

These hydroxides are less soluble in water as compared to the alkali metal hydroxides.

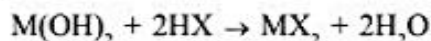
The solubility of the hydroxides in water increases with the increase in atomic number.  $Be(OH)_2$  and  $Mg(OH)_2$  are almost insoluble,  $Ca(OH)_2$  is sparingly soluble while  $Sr(OH)_2$  and  $Ba(OH)_2$  are increasingly more soluble.

- (v) **Halides.** Alkaline earth metals react with halogens directly to form halides having general formula,  $MX_2$ .

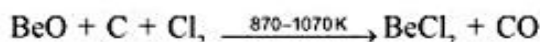




These halides can also be obtained by the action of halogen acids on metals, their oxides, carbonates and hydroxides.

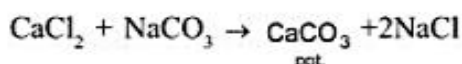


Beryllium chloride is prepared indirectly, from its oxide as follows:

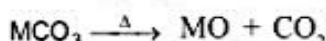


Beryllium chloride exists as monomer or dimer in vapour state but exists as polymer in solid state.

- (vii) **Carbonates.** Carbonates of alkaline earth metals are insoluble in water. These can be precipitated by addition of sodium or ammonium carbonate solution to the solution of salts of these metals. For example,

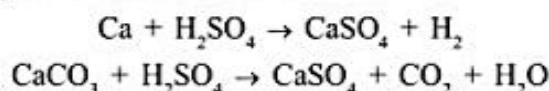


All the carbonates decompose on heating to give carbon dioxide and metals oxide.



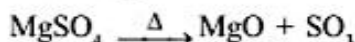
However, as the atomic number increases, the stability of the carbonates towards heat increases. Beryllium carbonate is unstable and can be kept only in an atmosphere of  $CO_2$ .

- (viii) **Sulphates.** Sulphates of alkaline earth metals can be prepared by the reaction of  $H_2SO_4$  with the metals, their oxides, hydroxides or carbonates.



The sulphates of alkaline earth metals are less soluble than the corresponding salts of alkali metals. Their solubilities decrease on going down the group.

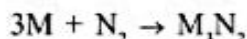
All these sulphates decompose on heating



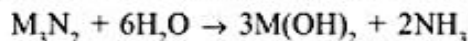
The thermal stability of sulphates increases on moving down the group from top to bottom.

**Lithopone:** Mixture of  $BaSO_4$  and  $ZnS$  is known as lithopone.

- (ix) **Nitrides.** Alkaline earth metals burn in nitrogen to form nitrides,  $M_3N_2$  which are ionic in nature.



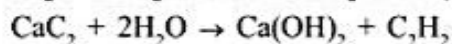
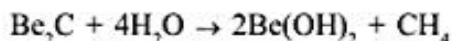
Nitrides on reactions with water are hydrolyzed and ammonia is released.



- (x) **Carbides.**  $BeO$  when heated with  $C$  at about  $2000^\circ C$ ,  $Be_2C$  is formed. The metals  $Mg$ ,  $Ca$ ,  $Sr$  and  $Ba$  form carbides of the formula  $MC_2$ . These carbides are formed when the metal or the metal oxide is heated with carbon in an electric furnace.

These carbides are ionic in nature.

$Be_2C$  yields methane on hydrolysis whereas carbides of other metals yield acetylene



- (xi) **Complex Compounds.** Alkaline earth metals have a tendency to form stable complexes. Their ability to form complexes is more as compared to alkali metals. This is because of the smaller size and higher charge of the alkaline earth metal ions as compared to alkali metal ions. Among the elements of group-2, beryllium and magnesium, have greater tendency of complexation.



## EXTRACTION OF ALKALINE METALS

### (1) Beryllium

**Occurrence :** (1) Beryl- $3\text{BeO}, \text{Al}_2\text{O}_3, 6\text{SiO}_2$  (2) Chrysoberyl -  $\text{BeO}, \text{Al}_2\text{O}_3$ .

**Extraction :**

The powdered beryl is treated with sulphuric acid when sulphates of beryllium and aluminium are formed from which aluminium sulphate is removed double sulphate by the addition of  $(\text{NH}_4)_2\text{SO}_4$ . Beryllium sulphate remaining solution is separated and calcined at high temperature to give  $\text{BeO}$ . The oxide is finally reduced to the metal by heating with carbon.

- Uses :** (1) In making alloys – a very small quantity of Be added to Mg increases casting power.  
 (2) It is highly permeable to X-rays and hence used for windows of X-ray tubes.  
 (3) In nuclear reactions as a source of neutrons, Bombarded with  $\alpha$ -particles, Beryllium gives neutrons.



### (2) Magnesium

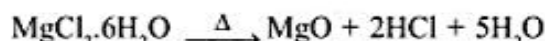
Important ores of magnesium are

- |  |  |
|--|--|
| (i) Magnesite, $\text{MgCO}_3$   | (ii) Dolomite, $\text{MgCO}_3 \cdot \text{CaCO}_3$       |
| (iii) Carnallite, $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ | (iv) Kieserite, $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ |

Sea water also contains magnesium salts. Magnesium content in sea – water is about 0.13%.

Magnesium is extracted by electrolysis of a molten mixture of anhydrous  $\text{MgCl}_2$ ,  $\text{NaCl}$  and  $\text{CaCl}_2$ . Anhydrous  $\text{MgCl}_2$  may be obtained from sea water or from carnallite.

**Anhydrous  $\text{MgCl}_2$**  is prepared from hydrated  $\text{MgCl}_2$  ( $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ) by passing a current of dry  $\text{HCl}$  gas over it. Anhydrous  $\text{MgCl}_2$  cannot be prepared by direct heating because it results in formation of  $\text{MgO}$  which is refractory



During electrolysis, the following reactions take place.



At cathode :  $\text{Mg}^{2+} + 2\text{e}^- \rightarrow \text{Mg}$

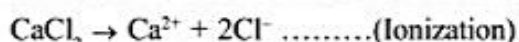
At anode :  $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$

### (3) Calcium

**Ores of Calcium**

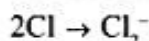
- |   |                                  |  |
|---|----------------------------------|--|
| (i) Gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ | (ii) Lime stone, $\text{CaCO}_3$ | (iii) Marble, $\text{CaCO}_3$                      |
| (iv) Fluorspar, $\text{CaF}_2$                        | (v) Anhydrite, $\text{CaSO}_4$   | (vi) Dolomite, $\text{CaCO}_3 \cdot \text{MgCO}_3$ |

Calcium is prepared by the electrolysis of a fused mixture of anhydrous calcium chloride and calcium fluoride. On passing electric current, calcium is liberated at the cathode.



At cathode :  $\text{Ca}^{2+} + 2\text{e}^- \rightarrow \text{Ca}$

At anode :  $\text{Cl}^- \rightarrow \text{Cl} + \text{e}^-$



### Anomalous behaviour of Be and its diagonal relationship with Al

Anomalous behaviour of Be and its diagonal relationship with Al is illustrated by the following points:

- Unlike group -2 elements but like aluminium, beryllium forms covalent compounds.
- The hydroxides of beryllium,  $[\text{Be}(\text{OH})_2]$  and aluminium,  $[\text{Al}(\text{OH})_3]$  are amphoteric in nature, whereas those of other elements of group -2 are basic in nature.
- Beryllium and aluminium forms fluoro complexes in solution.
- The oxides of both Be and Al, i.e.,  $\text{BeO}$  and  $\text{Al}_2\text{O}_3$  are high melting insoluble solids.
- $\text{BeCl}_2$  like  $\text{Al}_2\text{Cl}_6$  has a bridged polymeric structure.
- The salts of beryllium as well as aluminium are extensively hydrolyzed.
- Be, like Al, is rendered passive by concentrated  $\text{HNO}_3$ .
- Be forms many complex like Al
- Be and Al react with  $\text{NaOH}$  solution liberating  $\text{H}_2$ .
- $\text{Be}_2\text{C}$  and  $\text{Al}_4\text{C}_3$  react with water to give methane.
- Halides of the two elements have similar solubilities.
- The two metals do not impart colour to the Bunsen flame.

### Illustration

1. Which of the following elements will form a compound with oxygen in which one atom of the element is combined with one atom of oxygen to form an oxide of formula  $\text{MO}$  ?

(A) Be (B) Ne (C) Al (D) Cl

Ans. (A)

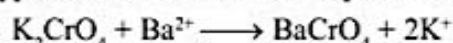
Sol. Be forms  $\text{BeO}$ , Al forms  $\text{Al}_2\text{O}_3$ , Cl forms  $\text{Cl}_2\text{O}_7$ ,  $\text{Cl}_2\text{O}$ ,  $\text{ClO}_2$  etc. while Ne does not react.

2. The cation which gives a yellow precipitate with potassium chromate is

(A)  $\text{SrCO}_3$  (B)  $\text{BaCO}_3$  (C)  $\text{CaCO}_3$  (D)  $\text{MgCO}_3$

Ans. (B)

Sol. Barium gives a yellow ppt. of barium chromate with pot. chromate.



### Exercise

1. The atom with atomic number 12 will most likely combine chemically with the atom whose atomic number is

(A) 3 (B) 10 (C) 11 (D) 16

Ans. (D)

2. A piece of magnesium ribbon was heated to redness in an atmosphere of nitrogen and then cooled with water. The gas evolved is

(A) Ammonia (B) Hydrogen (C) Nitrogen (D) Oxygen

Ans. (A)

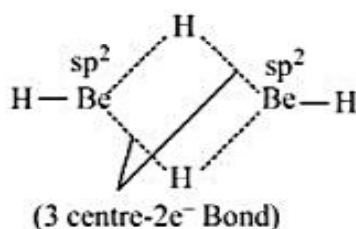
## COMPOUND OF ALKALINE EARTH METALS

### (1) Beryllium

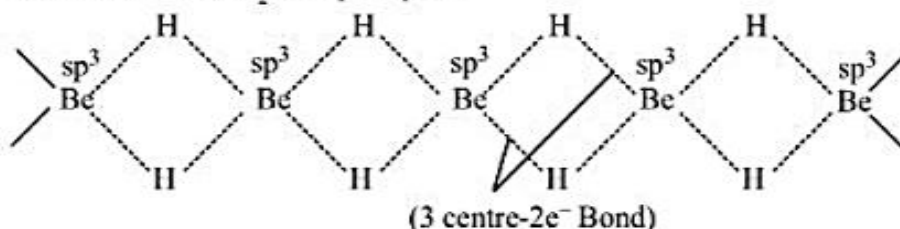
- (i) **Oxides and hydroxides :** Be forms only the monoxides: all others form monoxide and peroxide (eg. BaO, BaO<sub>2</sub>). The basic nature of the oxides and hydroxides of the metals increases down the group. BeO is amphoteric, CaO, SrO and BaO are basic. All these oxides dissolve in H<sub>2</sub>O giving the hydroxide (BeO is nearly insoluble). BeO dissolves in acids and alkalies to give salts.

(BeO) + 2HCl  $\longrightarrow$  BeCl<sub>2</sub> + H<sub>2</sub>O; BeO + 2NaOH  $\longrightarrow$  Na<sub>2</sub>BeO<sub>2</sub> + H<sub>2</sub>O.) The solubility of the hydroxides increase from Be to Ba. Ba(OH)<sub>2</sub> (Baryta) is moderately soluble in water.

- (ii) **Hydrides :** BeH<sub>2</sub> is covalent. MgH<sub>2</sub> is partially covalent and the remaining hydrides are largely ionic. BeH<sub>2</sub> is a polymeric solid, involving hydrogen bridging.

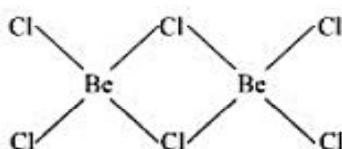


Dimer form of BeH<sub>2</sub> in vapour phase



Polymeric Form of BeH<sub>2</sub>, in solid state

- (iii) **Halides :** II group metals when heated with halogens, give the halides. Beryllium halides (eg. BeF<sub>2</sub> and BeCl<sub>2</sub>) are covalent due to the small size of Be<sup>2+</sup> (see Fajan's rules) and hence have comparatively low melting points and boiling points. The chlorides and fluorides of the other metals of the group are ionic solids. BeCl<sub>2</sub> in the solid state is polymeric containing chains of the form.



In the vapour state at high temperature BeCl<sub>2</sub> is a monomer.

The halides are deliquescent and they form hydrated salts. The solubility of halides in water decrease down the group from Ca to Ba.

- (iv) **Sulphates :** BeSO<sub>4</sub> is slightly soluble in water. The solubility of the sulphates of the metals decreases down the group. BaSO<sub>4</sub> and RaSO<sub>4</sub> are practically insoluble.



[**Note :** The solubility of an ionic solid in water depends on the lattice energy of the solid and the hydration energy for the ions of the solid. A large value of the former would lower the solubility, while a large value of the latter would increase the solubility. In the case of II group sulphates, the hydration energy factor has a dominant role. Since the hydration of ion decreases from,  $\text{Be}^{2+}$ , to  $\text{Ba}^{2+}$ , the solubility of the II group sulphates decreases down the group. For the fluorides and hydroxides of this group, the lattice energy has a dominant role and hence the solubility of these salts increases down the group.]

(v) **Carbonates and bicarbonates :** The carbonates of alkaline earth metals are insoluble in water: the bicarbonates are soluble. The carbonates and bicarbonates decompose on heating to give  $\text{CO}_2$  gas.

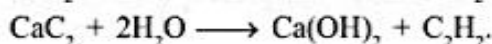
(vi) **Carbides** of II group metal are ionic carbides, which may be in a methanide or acetylide or allylide.  
**Beryllium Carbide :**

$\text{Be}_2\text{C}$  (methanide) reacts with water to give methane.



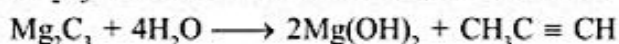
**Calcium Carbide :**

$\text{CaC}_2$  (acetylide) is decomposed by  $\text{H}_2\text{O}$  to give acetylene.



**Magnesium Carbide :**

$\text{Mg}_2\text{C}_3$  (allylide) reacts with water to give allylene (methyl acetylene).



(vii) **Nitrides :**

Example :  $\text{Mg}_3\text{N}_2$  – decomposed by  $\text{H}_2\text{O}$ , liberating  $\text{NH}_3$ .



**Complexes :** Be is the best complexing agent in this group. The complexing tendency decrease down the group.  $\text{Mg(Oxine)}_2$  is the complex formed by  $\text{Mg}^{2+}$  with 8 hydroxy quinoline(Oxine) and this forms the basis of quantitative estimation of Mg.

### Illustration

1. A metal M readily forms water soluble sulphate  $\text{MSO}_4$ , water insoluble hydroxide  $\text{M(OH)}_2$  and oxide MO which becomes inert on heating. The hydroxide is soluble in NaOH. The M is  
(A) Be (B) Mg (C) Ca (D) Sr

Ans. (A)

Sol.  $\text{Be(OH)}_2$  is amphoteric in nature so it is soluble in NaOH.

### Exercise

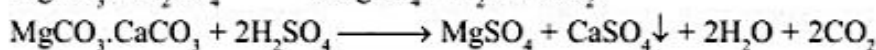
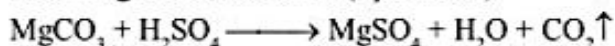
1. Amongst the following hydroxides, the one which has the lowest value of  $K_{sp}$  at ordinary temperature is:  
(A)  $\text{Mg(OH)}_2$  (B)  $\text{Ca(OH)}_2$  (C)  $\text{Ba(OH)}_2$  (D\*)  $\text{Be(OH)}_2$

Ans. (D)

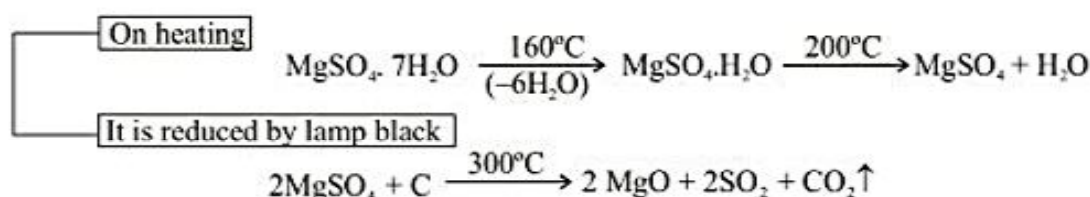


**(2) Magnesium****(i). Magnesium Sulphate ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ) epsom salt****Preparation :**

From magnesite or dolomite (Epsom salt)

**Physical properties :**

Colourless, efflorescent crystalline substance which forms a number of hydrate

**Chemical properties :****USES :**

1.  $\text{MgSO}_4$  is manufactured by dissolving keiserite ( $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ ) in boiling water & then crystallising the solution.
2.  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  is called as Epsom salt & shows deliquescence efflorescence & has purgative action.
3. Platinized  $\text{MgSO}_4$  is used as catalyst in Grillo's process for manufacture of  $\text{H}_2\text{SO}_4$ .

**(ii) Magnesium Chloride  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$** 

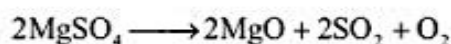
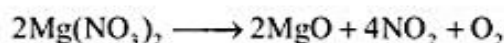
Magnesium chloride can be prepared by fractional crystallization of carnallite,  $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ . It can also be obtained from sea water. Magnesium salts present in sea-water are precipitated as  $\text{Mg}(\text{OH})_2$  by adding lime. The precipitate is filtered and dissolved in  $\text{HCl}$  solution. The solution on crystallization yields crystals of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ .



A mixture of magnesium chloride and magnesium oxide is known as **Sorel cement** or **magnesium cement**. This mixture reacts with water and sets into a solid mass having composition

**(iii) Magnesium Oxide ( $\text{MgO}$ )**

**Preparation:** It is prepared by burning  $\text{Mg}$  in air, by heating hydroxide, nitrate, sulphate or carbonate. Oxide prepared by heating magnesite ( $\text{MgCO}_3$ ) is called **calcined magnesia**.



**Properties:**

- (i) Magnesium oxide is a light white powder, which is highly infusible (m.p. 2800°C), and only slightly soluble in water.
- (ii) It is a basic oxide and hence reacts with acids to form salts.



- (iii) It is reduced by carbon at very high temperature to form magnesium carbide.



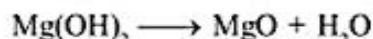
- (iv) It dissolves in aqueous solution of magnesium chloride or bromide forming basic salts such as  $\text{MgCl}_2 \cdot 9\text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$ .

**(iv) Magnesium Hydroxide ( $\text{Mg}(\text{OH})_2$ )**

**Preparation:** It is obtained by adding caustic soda solution to a solution of magnesium sulphate or chloride.

**Properties:**

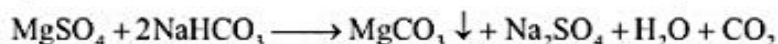
- (i) It is converted into its oxide on heating.



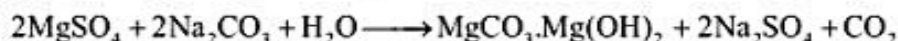
- (ii) It dissolves in  $\text{NH}_4\text{Cl}$  solution easily.

**(v) Magnesium Carbonate, ( $\text{MgCO}_3$ ):** It occurs in nature as magnesite,  $\text{MgCO}_3$  and dolomite,  $\text{MgCO}_3 \cdot \text{CaCO}_3$ .**Preparation:**

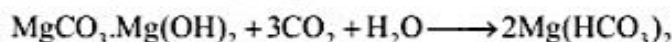
- (i) By adding sodium bicarbonate solution to a hot solution of magnesium salt.



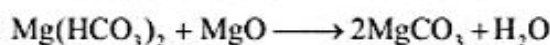
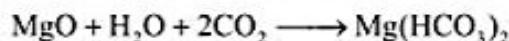
In case  $\text{Na}_2\text{CO}_3$  is used in place of  $\text{NaHCO}_3$ , a basic carbonate is obtained.



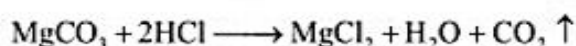
When  $\text{CO}_2$  gas is passed through the suspension of basic carbonate, magnesium bicarbonate is formed which on heating forms  $\text{MgCO}_3$ .



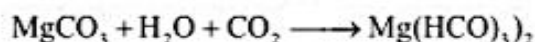
- (ii) Pure magnesium bicarbonate and hence carbonate can be prepared by passing  $\text{CO}_2$  through suspension of magnesium oxide in water.

**Properties:**

- (i) Magnesium carbonate is a white powder, insoluble in water.
- (ii) It dissolves in acids forming salts.

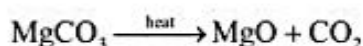


- (iii) Its aqueous solution also dissolves on passing a current of carbon dioxide because of the formation of  $\text{Mg}(\text{HCO}_3)_2$ , a temporary hardness causing substance.



A solution of magnesium bicarbonate containing 12 gm. of the salt per 100 ml is known as fluid magnesia.

- (iv) It decomposes on heating to form magnesium oxide.



#### 6. Sorel cement.

Magnesium oxide when mixed with a saturated solution of magnesium chloride sets to a hard mass like cement known as magnesia cement or Sorel cement. The composition is



- \*  $\text{Mg}(\text{ClO}_4)_2$  is known as anhydron

#### Illustration

1. Magnesium burns in  $\text{CO}_2$  to form  
 (A)  $\text{MgO} + \text{C}$                       (B)  $\text{MgO} + \text{CO}$                       (C)  $\text{MgCO}_3$                       (D)  $\text{MgO}$

Ans. (A)

Sol. Mg burns in  $\text{CO}_2$  to give  $\text{MgO}$  and  $\text{C}$ .

2. Which of the following is incorrect?  
 (A) Mg burns in air releasing dazzling light rich in UV rays  
 (B)  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  when mixed with ice gives freezing mixture  
 (C) Mg cannot form complexes  
 (D) Be can form complexes due to its very small.

Ans. (C)

Sol. Mg can form complexes and chlorophyll is one of such examples.

#### Exercise

1. Flame test is not given by  
 (A) Be                      (B) Mg                      (C) Ca                      (D) Sr

Ans. (A, B)

2. Pure anhydrous  $\text{MgCl}_2$  can be prepared from the hydrated salt by  
 (A) Heating the hydrate with coke                      (B) Heating the hydrate with Mg ribbon  
 (C) Melting the hydrate  
 (D) Heating the hydrate to red heat in an atmosphere of  $\text{HCl}$  gas

Ans. (D)

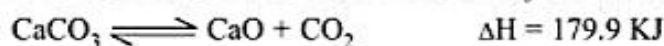


### (3) Calcium

#### (i) Calcium oxide Quick lime, Burnt lime (CaO).

##### Preparation

It is prepared by heating lime stone ( $\text{CaCO}_3$ ) at  $800^\circ\text{C}$



##### Condition for Good Yield :

- (i) Since the reaction is reversible, therefore the carbon dioxide formed must be removed as soon as it is formed so that the reaction remain in the forward direction.
- (ii) Temperature should not be allowed to rise above  $1270\text{K}$  otherwise silica ( $\text{SiO}_2$ ) present as impurity in limestone will react with  $\text{CaO}$  to form  $\text{CaSiO}_3$ .

##### Properties

- (i) Action of water :  

$$\text{CaO} + \text{H}_2\text{O} \longrightarrow \text{Ca(OH)}_2 + 15000 \text{ Caloric}$$

(quick lime)                      (Slaked lime)

Paste of lime in water is called milk of lime, while its hydrate is known as lime water.
- (ii) With moist chlorine :  

$$\text{CaO} + \text{Cl}_2 \longrightarrow \text{CaOCl}_2 \text{ (Bleaching powder)}$$
- (iii) When heated with carbon, it forms calcium carbide.  

$$\text{CaO} + 3\text{C} \xrightarrow{2000^\circ\text{C}} \text{CaC}_2 + \text{CO}$$

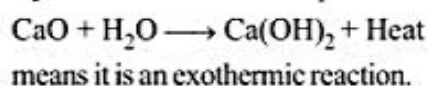
##### Uses

- (i) In purification of sugar
- (ii) As basic lining in furnances.

#### (ii) Calcium hydroxide, Slaked lime $\text{Ca(OH)}_2$ .

##### Preparation

By the action of water on quick lime.



##### Properties

- (i) Sparingly soluble in water and its solubility decreases with increases in temperature.
- (ii) Action of  $\text{CO}_2$  : Lime water turns milky on passing  $\text{CO}_2$  gas  

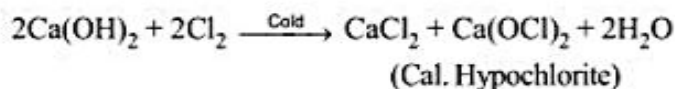
$$\text{Ca(OH)}_2 + \text{CO}_2 \longrightarrow \text{CaCO}_3 + \text{H}_2\text{O}$$

(Milkinsess)



(iii) Action of chlorine :

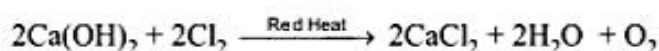
(a) Cold Condition :



(b) Below 35°C :  $3\text{Ca(OH)}_2 + 2\text{Cl}_2 \xrightarrow[35^\circ\text{C}]{\text{below}} \text{CaOCl}_2 + \text{H}_2\text{O}$

(c) On gentle Heating :  $6\text{Ca(OH)}_2 + 6\text{Cl}_2 \xrightarrow{\text{Heat}} 5\text{CaCl}_2 + \text{Ca(ClO}_3)_2 + 6\text{H}_2\text{O}$

(d) On Red Hot :



(iv) Action of Ammonia :

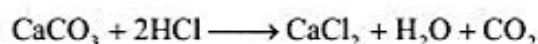


### Uses

- (i) For softening of hard water.
- (ii) For purification of sugar and coal gas.
- (iii) In preparation of bleaching powder, white wash, plaster etc.

(iii) **Calcium Carbonate, (CaCO<sub>3</sub>):** Calcium carbonate is found in nature as limestone, marble, coral, ice land spar, calcite, chalk, dolomite, etc.

**Preparation:** It is prepared as a white powder, known as precipitated chalk by dissolving marble or limestone in hydrochloric acid followed by precipitation with sod. or ammonium carbonate.

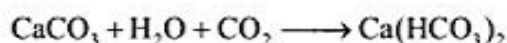


In the laboratory, it is prepared by passing CO<sub>2</sub> through lime-water or by adding sod. or ammo. carbonate solution to CaCl<sub>2</sub>.



### Properties:

- (i) It is a white powder and exists in two crystalline forms: calcite and aragonite.
- (ii) It is insoluble in water but dissolves in the presence of CO<sub>2</sub> due to the formation of calcium bicarbonate.



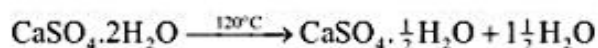
- (iv) **Calcium Bicarbonate, (Ca(HCO<sub>3</sub>)<sub>2</sub>):** It does not exist in solid state. However, its solution can be prepared by passing CO<sub>2</sub> gas through a suspension of calcium carbonate in water. On warming, it decomposes to calcium carbonate along with the evolution of carbon dioxide gas.
- (v) **Calcium Sulphate, (CaSO<sub>4</sub>):** It occurs in nature as anhydride (CaSO<sub>4</sub>) and gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O).

**Preparation:** It may be prepared by adding dilute sulphuric acid or soluble sulphate (e.g. Na<sub>2</sub>SO<sub>4</sub>) to the solution of a calcium salt.

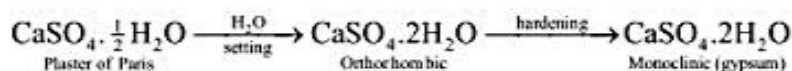


**Properties:**

- (i) It is a white crystalline solid. Like slaked lime, it is sparingly soluble in cold water and its solubility decreases further with the increase in temperature.
- (ii) It dissolves much more readily in dilute acids, even in acetic acid than in water. It dissolves also in ammonium sulphate solution forming  $\text{CaSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot \text{H}_2\text{O}$ .
- (iii) Monoclinic crystals of gypsum when heated, first changes into orthorhombic form without any loss of water. On further heating to  $120^\circ\text{C}$ , it loses three-fourth of its water of crystallization and forms the hemihydrate,  $(2\text{CaSO}_4) \cdot \text{H}_2\text{O}$  or  $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$  which is commonly known as Plaster of Paris.



Plaster of Paris is a white powder which when mixed with water takes up the water of crystallization again, thus converted back into the dehydrate and sets to a hard mass with slight expansion. Setting takes about 10–15 minutes and may be catalysed by the addition of common salt or delayed by the use of alum or borax.



Plaster of paris or gypsum when heated to about  $200^\circ\text{C}$  is converted into anhydrous calcium sulphate. The anhydrous form (anhydrite) is known as dead burnt because it does not set like Plaster of Paris when moistened with water.

**(vi) Calcium Chloride ( $\text{CaCl}_2$ )**

**Preparation:** It separates out as deliquescent crystals when a solution of lime or calcium carbonate in HCl is evaporated.

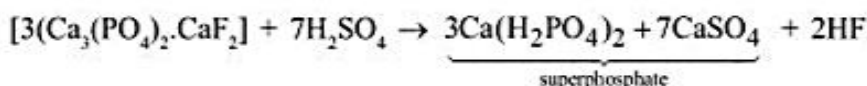


But it separates out from the reaction mixture as  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ . The anhydrous salt is obtained on heating above  $200^\circ\text{C}$ .

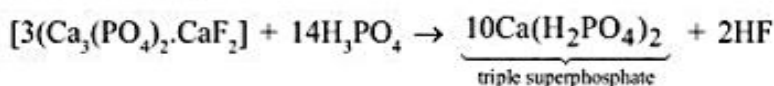
**Properties:** It is a colourless, deliquescent salt, highly soluble in water. The anhydrous salt is an excellent drying agent.

**(vii) Superphosphate**

Phosphate rocks such as fluoroapatite  $[3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2]$  are very insoluble, and thus are of no use to plants. Superphosphate is made by treating phosphate rock with concentrated  $\text{H}_2\text{SO}_4$ . The acid salt  $\text{Ca}(\text{H}_2\text{PO}_4)_2$  is more soluble, and over a period of weeks the superphosphate will dissolve in the soil water

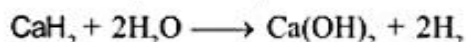


“Triple superphosphate” is made in a similar way, using  $\text{H}_3\text{PO}_4$  to avoid the formation of the waste product  $\text{CaSO}_4$ .

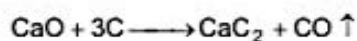


**(viii) Hydrolith**

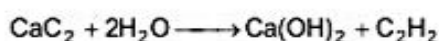
$\text{CaH}_2$  is technically called hydrolith and use on large scale for the production of hydrogen

**(ix) Calcium Carbide,  $\text{CaC}_2$** 

Calcium carbide is prepared by heating quick lime with coke in an electric furnace.



$\text{CaC}_2$  on reaction with water produces acetylene gas

**Illustration**

1. Which of the following substance is used as dehydrating agent in laboratory

(A) Calcium chloride (B) Sodium chloride (C) Sodium carbonate (D) Potassium nitrate

Ans. (A)

Sol.  $\text{CaCl}_2$  because it is hygroscopic.

2. Setting of plaster of paris is

(A) Oxidation with atmospheric  $\text{CO}_2$

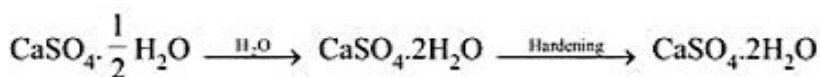
(B) Combination with atmospheric  $\text{CO}_2$

(C) Dehydration

(D) Hydration to yield another

Ans. (D)

Sol. Setting of plaster of paris is



orthorhombic

Mono orthorhombic Gypsum

The setting is due to formation of another hydrate.

**Exercise**

1. Which of the following statements is false

(A)  $\text{CaOCl}_2$  gives  $\text{OH}^-$ ,  $\text{Cl}^-$  and  $\text{OCl}^-$  in aqueous solution

(B) Diamond and graphite are allotrops

(C) Bleaching action of  $\text{Cl}_2$  is moist condition is not permanent

(D) Calomel is  $\text{Hg}_2\text{Cl}_2$

Ans. (C)







**Sol.** The ionisation potential value of Lithium is maximum among alkali metals i.e., its tendency to ionise to give  $\text{Li}^+$  ions should be the minimum i.e. Li should be the poorest reducing agent. But, lithium is the strongest reducing agent. This is due to the largest value of hydration energy of  $\text{Li}^+$  ions.

**Q.11** Which liberates ammonia when treated with

- (A)  $\text{Li}_3\text{N}$  (B)  $\text{Mg}_3\text{N}_2$  (C)  $\text{CaCN}_2$  (D) All

**Ans.** (D)

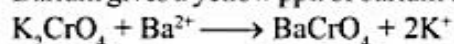
**Sol.** All nitrides react with  $\text{H}_2\text{O}$  to yield  $\text{NH}_3$ . Calcium cyanamide ( $\text{CaCN}_2$ ) on hydrolysis also given  $\text{NH}_3$ .  
 $\text{CaNCN} + 3\text{H}_2\text{O} \longrightarrow \text{CaCO}_3 + \text{NH}_3$

**Q.12** The cation which gives a yellow precipitate with potassium chromate is

- (A)  $\text{SrCO}_3$  (B)  $\text{BaCO}_3$  (C)  $\text{CaCO}_3$  (D)  $\text{MgCO}_3$

**Ans.** (B)

**Sol.** Barium gives a yellow ppt. of barium chromate with pot. chromate.



**Q.13** If  $\text{Na}^+$  ion is larger than  $\text{Mg}^{2+}$  ion and  $\text{S}^{2-}$  ion is larger than  $\text{Cl}^-$  ion, which of the following will be least soluble in water?

- (A) Sodium chloride (B) Sodium sulphide (C) Magnesium chloride (D) Magnesium sulphide

**Ans.** (D)

**Sol.** Magnesium sulphide. Higher the lattice energy lower the solubility. Out of the four combinations possible, the lattice energy of  $\text{MgS}$  (Bi-bivalent ionic solid) is higher than those of  $\text{Na}_2\text{S}$ ,  $\text{MgCl}_2$  (uni-bivalent or biunivalent ionic solids) and  $\text{NaCl}$  (uniunivalent ionic solids) and hence  $\text{MgS}$  is the least soluble.

**Q.14** Which of the following is used as barium meal for getting the X-ray spectrum of the human digestive system?

- (A)  $\text{BaSO}_4$  (B)  $\text{BaCl}_2$  (C)  $\text{BaF}_2$  (D)  $\text{BaCO}_3$

**Ans.** (A)

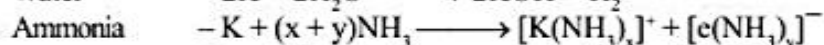
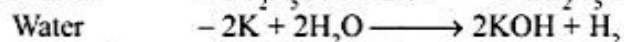
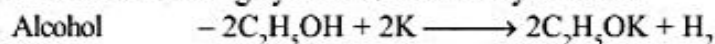
**Sol.**  $\text{BaSO}_4$  is both insoluble in water and opaque to X-rays and hence is used to get the X-ray spectrum of the digestive system?

**Q.15** Potassium is kept in

- (A) Alcohol (B) Water (C) Kerosene (D) Liquid ammonia

**Ans.** (C)

**Sol.** Alkali metals are highly reactive metal. They react with



Ammoniated cation

Ammoniated electron

But they do not react with Kerosene.

## p - BLOCK-I

The elements in which the last electron enters to the outer most p orbital are called p- block elements. As the maximum number of electrons that can be accommodated in a set of p-orbitals is six, therefore there are six groups of p - blocks in the periodic table.

### Group 13 Elements : Boron Family

The Elements are B (Non metal), Al, Ga, In, Tl (Metals)

General electronic configuration [Noble gas]  $ns^2 np^1$

#### Atomic and Physical properties

(i) **Atomic and Ionic radii**

Atomic radii:  $B > Ga < Al < In < Tl$

(ii) **Ionization Enthalpies.**

$B > Tl > Ga > Al > In$  (Sum of three IE values)

(iii) **Melting and Boiling points**

M.P.  $B > Al > Tl > In > Ga$

B.P.  $B > Al > Ga > In > Tl$

(iv) **Electropositive Character**

Due to high IE they are less electropositive. On moving down the group metallic character increases due to decrease in IE [  $\therefore$  B is nonmetal and other elements are metals.]

$B <$	$Al < Ga < In < Tl$
Non metal	Metals

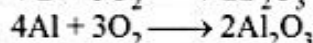
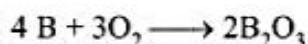
**Note :** Boron exists in many allotropic forms. All the allotropes have basic building  $B_{12}$  icosahedral units made up of polyhedron having 20 faces and 12 corners. For example one is the simplest form :  $\alpha$  - rhombohedral boron.



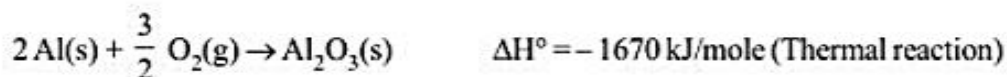
But Al, In & Tl all have close packed metal structure.

#### CHEMICAL PROPERTIES

(i) **Reaction with oxygen**

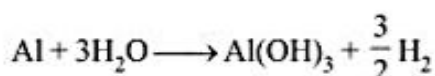
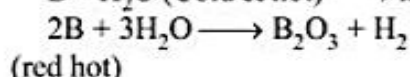
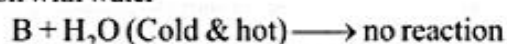


Al should react air to form a very thin oxide film ( $10^{-4}$  to  $10^{-6}$  mm thick) on the surface and protects the metal from further attack

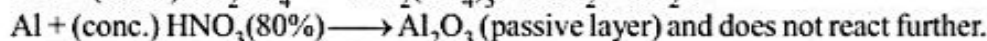
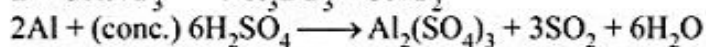
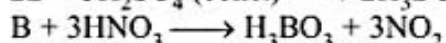
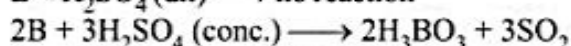
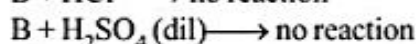
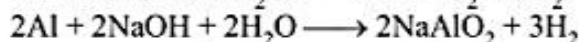




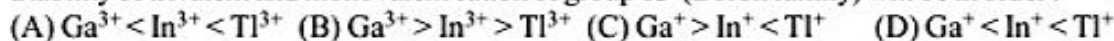
## (ii) Reaction with water



Ga and In are attacked neither by cold water nor hot water unless oxygen is present. Tl form an oxide on surface.

(iii)  $\text{B} + \text{HCl} \longrightarrow \text{no reaction}$ (iv)  $2\text{B} + 2\text{NaOH} + 2\text{H}_2\text{O} \longrightarrow 2\text{NaBO}_2 + 3\text{H}_2$ (v)  $2\text{B} + \text{N}_2 \longrightarrow 2\text{BN}$        $2\text{Al} + \text{N}_2 \longrightarrow 2\text{AlN}$ (vi)  $3\text{Mg} + 2\text{B} \longrightarrow \text{Mg}_3\text{B}_2$ **Illustration**

1. Stability of trivalent and monovalent cation of group 13 (Boron family) will be in order :



Ans. (B), (D)

Sol. By inert pair effect stability of +3 state decreases and that of +1 state increases along a group.

**Exercise**

1. Which one of the following elements has the highest melting point

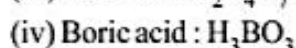
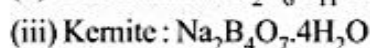
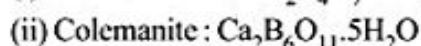
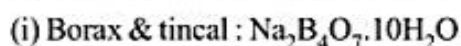


Ans. (B)

**BORON AND ITS COMPOUNDS**

## (i) Occurrence :

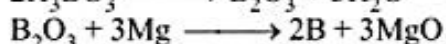
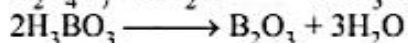
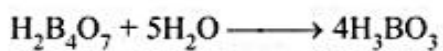
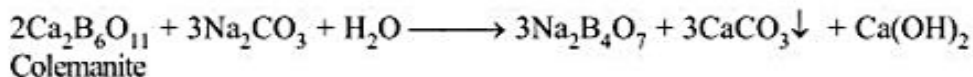
Boron does not occur free in nature .It occurs principally as borates e.g.



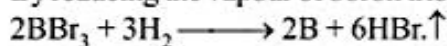


**(ii) Extraction of Boron** →**Extraction from minerals :**

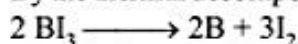
Principle → Boron may be obtained by treating borax with hot concentrated HCl, igniting the boric acid  $\text{H}_3\text{BO}_3$  to give the oxide  $\text{B}_2\text{O}_3$  and finally reduced with Mg.

**Crystalline Boron :****Preparation :**

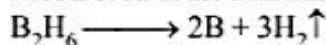
By reducing the vapour of boron tribromide ( $\text{BBr}_3$ ) with hydrogen in an electric arc



By the thermal decomposition of  $\text{BI}_3$  on a tantalum filament



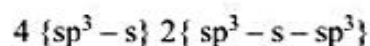
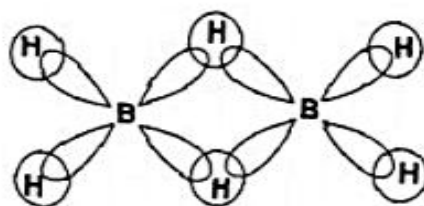
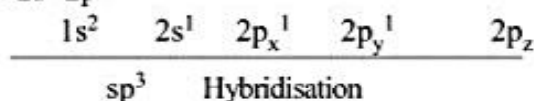
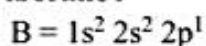
Pure Boron in the thin film can also be obtained by heating diborane to  $700^\circ\text{C}$

**(iii) Physical properties**

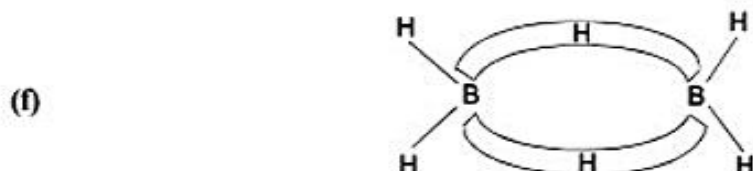
(a) It is a non-metal. Boron occurs in two different allotropic forms AMORPHOUS and CRYSTALLINE

(b) Amorphous boron has not been obtained in the pure state .

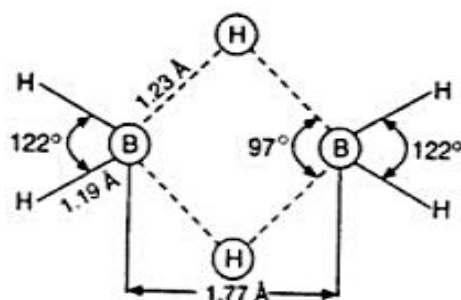
(c) Crystalline boron is a black powder , extremely hard with a metallic appearance but with very low electrical conductivity.

**COMPOUNDS OF BORON****(I)  $\text{B}_2\text{H}_6$  (Diborane)****Structure of Diborane :**

- (a) 4 Terminal H-are bonded by  $\sigma$  bond & remaining 2H are bridging hydrogens and of these are broken then dimer become monomer.
- (b) Boron undergoes  $sp^3$  hybridisation 3 of its  $sp^3$  hybridised orbitals contain one  $e^-$  each & fourth  $sp^3$  hybrid orbital is vacant
- (c) 3 of these  $sp^3$  hybrid orbitals get overlapped by s orbitals of 3 hydrogen atoms.
- (d) One of the  $sp^3$  hybrid orbitals which have been overlapped by s orbital of hydrogen gets overlapped by vacant  $sp^3$  hybrid orbital. of 2<sup>nd</sup> Boron atom and its vice versa.
- (e) By this two types of overlapping take place 4( $sp^3-s$ ) overlap bonds & 2 ( $sp^3-s-sp^3$ ) overlap bonds.



H is held in this bond by forces of attraction from B & This bond is called 3 centered two electron bonds. It is also called Banana bonds. Due to repulsion between the two hydrogen nuclei, the delocalised orbitals of bridges are bent away from each other on the middle giving the shape of banana.



#### Uses of Diborane :

- Diborane is used for preparing substances such as high energy fuel & propellents.
- Boron hydrides have been tried as rocket fuels .
- It is used as a catalyst in polymerisation reaction.
- It is used as a reducing agent in inorganic reaction.
- It is used for welding torches.

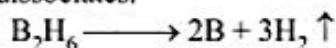
#### Preparation of $B_2H_6$ :

- $Mg_3B_2 + HCl \longrightarrow B_2H_6 + B_4H_{10} + B_5H_9$  etc.  
(10%)
- $B_4H_{10} \xrightarrow[100^\circ C]{\Delta} B_2H_6 + H_2 + \text{higher borane}$
- $BCl_3 \text{ (or } BBr_3) + 6H_2 \xrightarrow[\text{discharge at low pressure}]{\text{Electric}} B_2H_6 + 6HCl$
- $3LiAlH_4 + 4BF_3 \longrightarrow 3LiF + 3AlF_3 + 2B_2H_6$   
or  $LiBH_4$  or  $3(BF_3)$

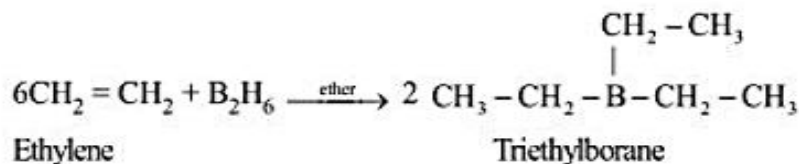
#### Physical properties :

- Diboranes ( Melting point =  $-165.5^\circ C$  , Boiling point =  $-92.5^\circ C$ ) is a colourless gas with a foul smell & is extremely toxic.
- It is an extremely reactive inflammable gas which burns in air with green flame.

- (iii) Diborane reacts with sodium amalgam to form an addition product  $B_2H_6Na_2$ .  
 (iv) On heating to  $700^\circ C$  diborane dissociates.



- (v) Diborane readily adds at  $0^\circ C$  to  $25^\circ C$  to the olefinic acetylene compound to form trialkylborane. The reaction is known as hydroboration.



- (vi) Diborane is electron - deficient molecule & hence it reacts with several molecule having lone pair(s) of electron (e.g. CO, ether, amines etc.) to form complex compounds.  
 (vii) Boranes have great affinity for water &  $O_2$  hence they do not occur in nature. Moreover borane cannot be prepared directly from its elements as they have positive enthalpy & positive free energy of formation.

### Chemical properties

- (i)  $B_2H_6 + O_2 \xrightarrow[\text{air spontaneously}]{\text{burns in}} B_2O_3 + H_2O$   
 (ii)  $B_2H_6 + H_2O \text{ (Cold)} \longrightarrow H_3BO_3 + 6H_2$   
 (iii)  $B_2H_6 + HCl \text{ (dry)} \xrightarrow[AlCl_3]{\text{anh.}} B_2H_5Cl + H_2$   
 (iv)  $B_2H_6 + 2N(CH_3)_3 \longrightarrow 2(CH_3)_3N + BH_3$   
 (v)  $B_2H_6 + 2Na \text{ (amalgam)} \longrightarrow B_2H_6Na_2$   
 (vi)  $6NH_3 + 3B_2H_6 \longrightarrow 2B_3N_3H_6 + 12H_2$   
borazole

### Illustration

1. In diborane  
 (A) 4-Bridged hydrogens and two terminal hydrogens are present  
 (B) 2-Bridged hydrogens and four terminal hydrogens are present  
 (C) 3-Bridged and three terminal hydrogens are present  
 (D) None of the above

Ans. (B)

Sol. In diborane ( $B_2H_6$ ) there are two bridged H atoms and four terminal H atoms which along with two B atoms lie in plane perpendicular to each other.

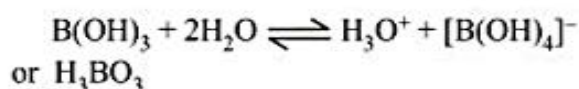
### Exercise

1. In the reaction  $B_2O_3 + C + Cl_2 \longrightarrow A + CO$ . The A is  
 (A)  $BCl_3$  (B)  $BCl_2$  (C)  $B_2Cl_2$  (D)  $CCl_2$   
 Ans. (A)

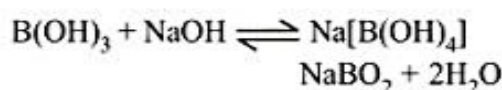


**(II) Orthoboric Acid ( $\text{H}_3\text{BO}_3$ )**

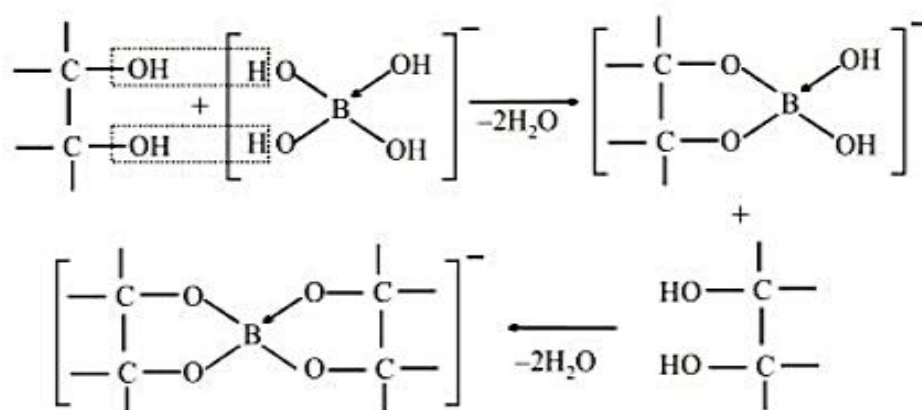
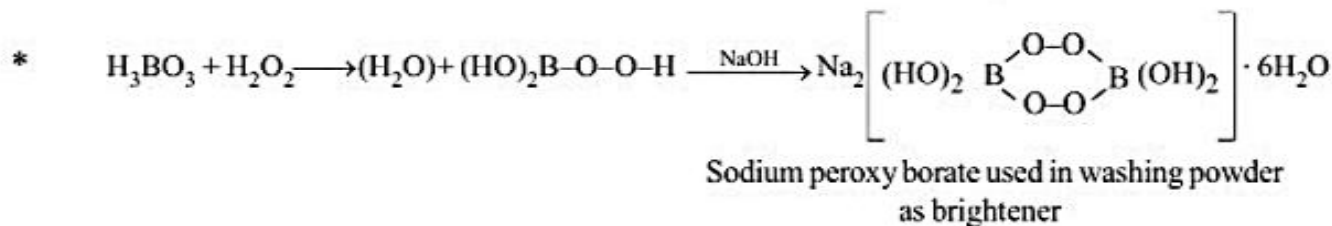
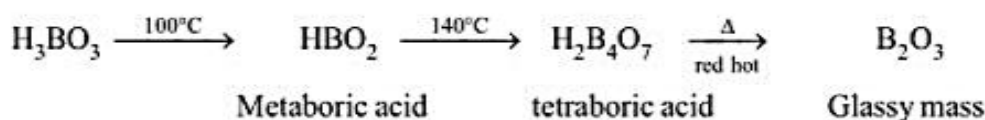
$\text{H}_3\text{BO}_3$  is soluble in water and behaves as weak monobasic acid. It does not donate protons but rather it accepts  $\text{OH}^-$ . Therefore it acts as a Lewis acid ( $\text{B}(\text{OH})_3$ )



Since  $\text{B}(\text{OH})_3$  only partially reacts with water to form  $\text{H}_3\text{O}^+$  and  $[\text{B}(\text{OH})_4]^-$  it behaves as a weak acid. Thus it cannot be titrated satisfactorily with  $\text{NaOH}$  as a sharp end point is not obtained. If certain polyhydroxy compounds such as glycerol, mannitol or sugar are added to the titration mixture then  $\text{B}(\text{OH})_3$  behaves as a strong monobasic acid and hence can now be titrated with  $\text{NaOH}$  and end point is diluted using phenolphthalein as indicator.



The added compound must be a cis diol to enhance the acidic properties. In this way the cis-diol forms very stable complexes with  $[\text{B}(\text{OH})_4]^-$  formed in forward direction above, thus effectively removing it from solution. Hence reaction proceeds in forward direction (Le-Chatelier principle.)

**\* Heating of boric acid :**



- Ans. (D)**

**Sol.**  $\text{Na}_2\text{B}_4\text{O}_7 + 7\text{H}_2\text{O} \longrightarrow 2\text{B(OH)}_3 + 2\text{Na[B(OH)}_4\text{]}$   
 $\text{B(OH)}_3$  or  $\text{H}_3\text{BO}_3$  is an acid and does not react with acid.  
Hence  $\text{Na[B(OH)}_4\text{]}$  reacts with acid.

### Exercise

1. Borax is converted into B by steps  
 Borax I  $\text{H}_3\text{BO}_3 \xrightarrow{\Delta} \text{B}_2\text{O}_3$  — II  $\rightarrow$  B  
 I and II reagents are :  
 (A) Acid, Al (B) Acid, C (C) Acid, Fe (D) Acid, Mg
- Ans. (D)

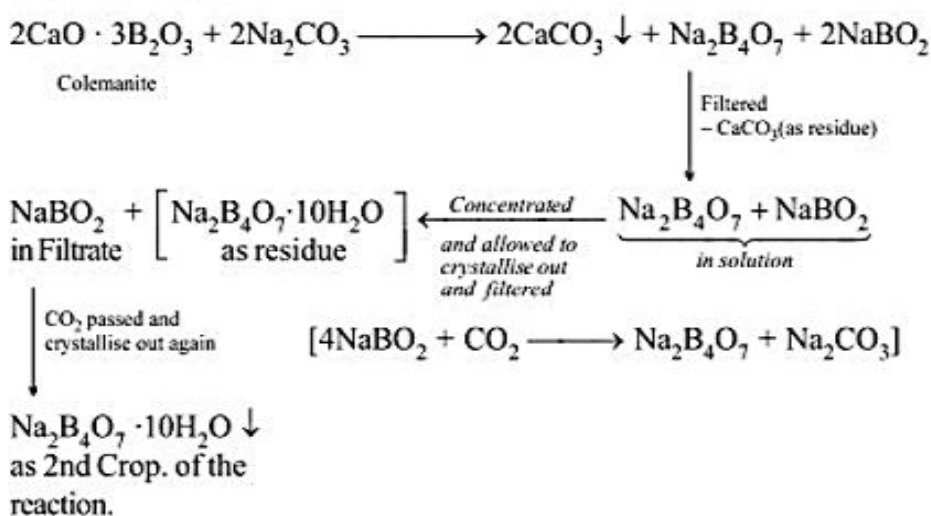
(III) Borax  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$  or Tincal :

- (a) It is also named as sodium tetra borate decahydrate.  
(b) Common Indian name is Suhaga.  
(c)  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$  is known as Jeweller's  
(d)  $\text{Na}_2\text{B}_4\text{O}_7$  is known as Boron glass

**(b) Preparation :**

**Form colemanite :**

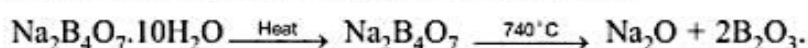
### Preparation of Borax :



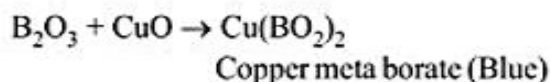
**Uses of borax:** (i) In making glass, enamel and glaze of pottery.  
(ii) As antiseptic in medicinal soaps preparation.

**Chemical Properties :****Action of Heat on Borax :**

- (i) Borax swells up on heating.  
 (ii) On heating borax loses water and swells into a white mass which on further heating melts to form transparent glassy solid called Borax glass and Borax bead.

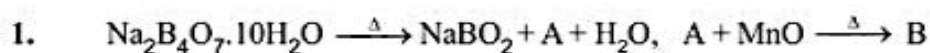


- (iii) The borax bead is due to the formation of  $\text{B}_2\text{O}_3$  which when fused with metal salts form corresponding metaborate.



- (iv) Colour of meta borates

Cu	Fe	Co	Ni	Cr
Blue	Green	Blue	Brown	Green

**Illustration**

A and B are :

(A)  $\text{Na}_3\text{BO}_3$ ,  $\text{Mn}_3(\text{BO}_3)_2$

(B)  $\text{Na}_2(\text{BO}_2)_2$ ,  $\text{Mn}(\text{BO}_2)_2$

(C)  $\text{B}_2\text{O}_3$ ,  $\text{Mn}(\text{BO}_2)_2$

(D) None is correct

Ans. (C)

Sol.  $\text{A} = \text{B}_2\text{O}_3$ ,  $\text{B} = \text{MnO} + \text{B}_2\text{O}_3 \rightarrow \text{Mn}(\text{BO}_2)_2$

**Exercise**

1. Borax is used as a buffer since :  
 (A) Its aqueous solutions contains equal amount of weak acid and its salt  
 (B) It is easily available  
 (C) Its aqueous solution contains equal amount of strong acid and its salt  
 (D) Statement that borax is a buffer, is wrong

Ans. (A)

**Aluminium and its compounds**

- Aluminium does not occur free in nature. It is most abundant metal in the earth's crust.
- Important minerals are :
 

(i) Bauxite : $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$	(ii) Diaspore : $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$
(iii) Corundum : $\text{Al}_2\text{O}_3$	(iv) Cryolite : $\text{Na}_3\text{AlF}_6$
(v) Feldspar : $\text{KAlSi}_3\text{O}_8$ or $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$	
- Among binary compounds of Al only  $\text{AlF}_3$  &  $\text{Al}_2\text{O}_3$  are ionic.
- Extraction of Al is done from bauxite ( $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ ) by electrolysis. The process involves:
 

(a) Purification of bauxite.	(b) Electrolytic reduction of alumina.
(c) Purification of Al.	
- Bauxite is associated with impurities of  $\text{Fe}_2\text{O}_3$ ,  $\text{SiO}_2$  &  $\text{TiO}_2$ . The method of purification depends upon the nature of impurity.

## COMPOUNDS OF ALUMINIUM

### (I) $\text{Al}_2\text{O}_3$ (Corundum)

#### Preparation :

- (i)  $2\text{Al}(\text{OH})_3 \xrightarrow{300^\circ\text{C}} \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O}$
- (ii)  $\text{Al}_2(\text{SO}_4)_3 \xrightarrow{\Delta} \text{Al}_2\text{O}_3 + 3\text{SO}_3$
- (iii)  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O} \xrightarrow{\Delta} \text{Al}_2\text{O}_3 + 2\text{NH}_3 + 4\text{SO}_3 + 25\text{H}_2\text{O}$

#### Properties

- (1) It is very stable and unreactive
- (2) Melting point  $\longrightarrow 2050^\circ\text{C}$   
Boiling point  $\longrightarrow 2980^\circ\text{C}$
- (3) It is amphoteric oxide :  

$$\text{Al}_2\text{O}_3 + 6\text{HCl} \longrightarrow 2\text{AlCl}_3 + 3\text{H}_2\text{O}$$

$$\text{Al}_2\text{O}_3 + 2\text{NaOH} \longrightarrow 2\text{NaAlO}_2 + \text{H}_2\text{O}$$
- (4) Reaction with carbon :  

$$2\text{Al}_2\text{O}_3 + 9\text{C} \xrightarrow{2000^\circ\text{C}} \text{Al}_4\text{C}_3 + 6\text{CO}$$

$$4\text{Al}(\text{OH})_3 + 3\text{CH}_4 \xleftarrow{12\text{H}_2\text{O}}$$

#### Uses :

- (i) It is used as a refractory material.
- (ii) In chromatography for separation of mixture.
- (iii) In preparation of Artificial gems.

### (II) $\text{AlCl}_3$

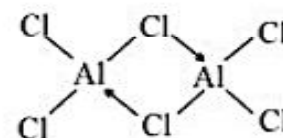
#### Preparation:

- (i)  $2\text{Al} + 6\text{HCl}(\text{vap.}) \xrightarrow[\text{dry}]{\text{(over heated)}} 2\text{AlCl}_3 + 3\text{H}_2$
- (ii)  $\text{Al}_2\text{O}_3 + 3\text{C} + 3\text{Cl}_2 \xrightarrow[1000^\circ\text{C}]{\Delta} 2\text{AlCl}_3(\text{vap.}) + 3\text{CO}$   

$$\downarrow \text{Cooled}$$
  
 Solid anh.  $\text{AlCl}_3$

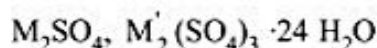
#### Props:

- (i) Its anhydrous form is deliquescent and fumes in air.
- (ii) It sublimes at  $180^\circ\text{C}$ .
- (iii) It is covalent and exists in the form of dimer even if in non polar solvents e.g. alc., ether, benzene, where it is soluble in fair extent.



- Uses:** (i) Friedel-Craft reaction  
(ii) Dyeing, drug. & perfumes etc.



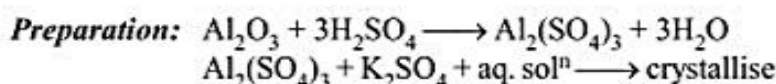
**(III) Alums:**

**Props:** Swelling characteristics

where  $M = Na^+, K^+, Rb^+, Cs^+, As^+, Tl^+, NH_4^+$

$M' = Al^{+3}, Cr^{+3}, Fe^{+3}, Mn^{+3}, Co^{+3}$

$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$	Potash alum
$(NH_4)_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$	Ammonium alum
$K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24H_2O$	Chrome alum
$(NH_4)_2SO_4 \cdot Fe_2(SO_4)_3 \cdot 24H_2O$	Ferric alum



**Uses:** (i) Act as coagulant (ii) Purification of water  
 (iii) Tanning of leather (iv) Mordant in dying (v) Antiseptic

**Illustration**

1. Generally the atomic and ionic radii increase with increase in atomic number down the group. But the atomic size of aluminium and gallium is almost the same. This is because  
 (A) The nuclear charge of Ga is higher than that of Al  
 (B) Gallium contains intervening d-electrons which do not screen the valence electrons effectively  
 (C) The ionization energies of Ga and Al are comparable  
 (D) All the three above.

**Ans. (B)**

**Sol.** Due to the poor shielding (screening) effect of d-electrons in case of Ga, the valence electrons are attracted more strongly and hence the size is not increased.

2. Which of the following statements is incorrect about aluminium ?  
 (A) It liberates  $H_2$  from acids (B) It liberates  $H_2$  from bases  
 (C) It liberates  $H_2$  from both acids and bases (D) It liberates  $H_2$  from acids but not from bases

**Ans. (D)**

**Sol.** Al liberates  $H_2$  from both acids and alkalies. For example,  
 $2Al + 6HCl \longrightarrow 2AlCl_3 + 3H_2$ ; also refer to.

**Exercise**

1. Which of the following reactions forms the basis of Goldschmidt aluminothermite process ?  
 (A)  $2Al + N_2 \longrightarrow 2AlN$  (B)  $2Al + 3Cl_3 \longrightarrow 2AlCl_3$   
 (C)  $2Al + 6HCl \longrightarrow 2AlCl_3 + 3H_2$  (D)  $2Al + Fe_2O_3 \longrightarrow Al_2O_3 + 2Fe$ .

**Ans. (D)**

2. Aluminium becomes passive in  
 (A) Conc.  $HNO_3$  (B)  $H_2CrO_4$  (C)  $HClO_4$  (D) All

**Ans. (D)**



## Group 14 Elements (Carbon Family)

*The Elements* are C [Non metals], Si, Ge [Metalloids], Sn, Pb, [Metals]

General electronic configuration [ noble gas]  $ns^2 np^2$

**(I) Atomic and Physical properties**

**(i) Atomic Radii**

Covalent radii :  $C < Si < Ge < Sn < Pb$

**(ii) Ionizations Enthalpies**

$C > Si > Ge > Pb > Sn$  ( $IE_1$  values)

**(iii) Melting and Boiling Points**

M.P.  $C > Si > Ge > Pb > Sn$

B.P.  $Si > Ge > Sn > Pb$

**(iv) Metallic Character**

$C < Si < Ge < Sn < Pb$  (Metallic character)

C, Si [Non metal]

Ge [Metalloid]

Sn, Pb [Metal]

**(II) Allotropes**

**Carbon have two types of Allotropic forms**

(1) Crystalline (2) Amorphous

**(1) Crystalline : Diamond, Graphite and Fullerene**

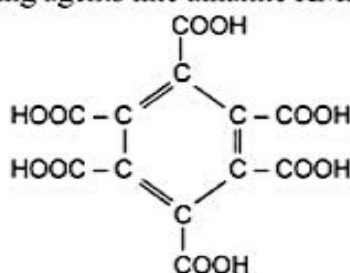
**(i) Diamond :**

- (1) Each carbon is linked to another atom and so very closed packing in structure of Diamond.
- (2) Density and hardness is very much greater for diamond because of closed packing in diamond due to  $sp^3$  hybrid and are tetrahedrally arranged around it.
- (3) Diamond has sharp cutting edges that's why it is employed in cutting of glass.
- (4) Diamond crystals are non conductor of electricity because of not presence of mobile electron.
- (5) 1 carat of diamond = 200 mgm.
- (6) Diamond powder if consumed is fatal and causes death in minutes.

**(ii) Graphite :**

- (1) In graphite carbon are  $sp^2$  hybridised and due to this carbon exist as hexagonal layer.
- (2) Each carbon is lined with 3 carbons and one carbon will be left and form a two dimensional shed like structure.
- (3) Distance between two layers is very large so no regular bond is formed between two layers. The layers are attached with weak vander waal force of attraction.
- (4) The carbon have unpaired electron so graphite is a good conductor of current.
- (5) C-C bond length in Graphite is shorter ( $1.42 \text{ \AA}$ ) than that of Diamond ( $1.54 \text{ \AA}$ ).
- (6) Graphite has high melting point so it is employed in manufacture of crucible.

- (7) Graphite when heated with oxidising agents like alkaline  $\text{KMnO}_4$  forms metallic acid.



Benzene hexa carboxylic acid

(iii) **Buck Minster Fullerene :**

- (1) It has the formula  $\text{C}_{60}$  and is made from interlocking hexagonal and pentagonal rings of carbon atoms.
- (2) Such molecules are now thought to exist even in chimney root or candle smoke.
- (3) The structure of  $\text{C}_{60}$  is similar to the surface of a football which has also set of interlocking hexagons and pentagons.
- (4) Another molecule  $\text{C}_{70}$  has been recently discovered.
- (5) These and similar large carbon molecules are sometimes referred as "bucky balls".

(2) **Amorphous Allotropic Forms of Carbon :**

(A) **Lamp Black :**

- (i) Obtained by incompletely combustion of compounds which contains higher % of carbon, benzene, turpentine, acetylene etc. These all on combustion form black carbon called lamp black.
- (ii) Black blue ink, printing ink, black paints, varnishes are made from lamp black.

(B) **Coke :**

- (i) Obtained by destructive distillation of coal
- (ii) Cake is usually employed as weak reducing agent with compared to CO.

(C) **Wood Charcoal :**

- (i) Obtained by incomplete combustion of wood.
- (ii) Used to decolourise organic compound.

**Allotropic forms of Tin :**

- (i) It has three allotropic forms
  - (a) White tin :
    - (i) Used in containers of oil.
    - (ii) White tin is more stable and having maximum density.
  - (b) Grey tin :
    - (c) Rhombic tin :
- (ii) At low temp. ( $18^\circ\text{C}$ ) white tin converts to Grey tin.
- (iii) At temp. of  $160^\circ\text{C}$  (above) white tin converts to Rhombic tin.
- (iv) White tin forms grey tin which is obtained as powdery substance and with formation of this thickness of white tin container decreases. This is called Tin pest or Tin disease or Tin plague.
- (v) When tin sheets are folded, they given a peculiar sound which is called as Tin cry.

**(3) Catenation**

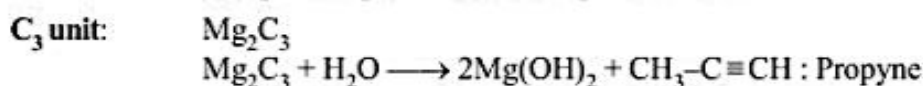
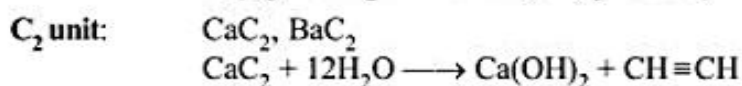
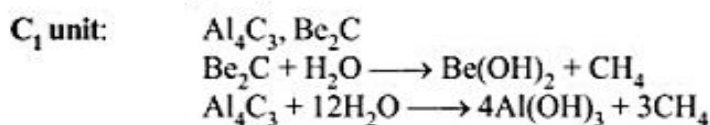
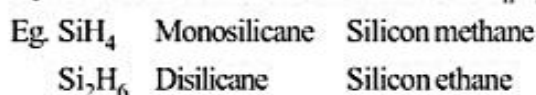
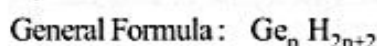
The property of forming bonds with atoms of the same element or tendency to self linking called catenation. Carbon shows maximum catenation. On moving down the group catenation tendency decreases. This because the strength of C – C bond is very high and in case of other elements, strength of M – M (where M = Si, Ge, Sn, Pb) bond is decreases down the group.

Bond	Bond Energy (kJmol <sup>-1</sup> )
C – C	348
Si – Si	297
Ge – Ge	260
Sn – Sn	240

**COMPOUNDS OF CARBON FAMILY****(1) Carbide****Types of Carbide****(i) Ionic and salt like:**

Classification on basis of  
no. of carbon atoms  
present in hydrocarbon  
found on their hydrolysis

- (a) C<sub>1</sub> unit  
(b) C<sub>2</sub> unit  
(c) C<sub>3</sub> unit

**(ii) Covalent carbide : SiC & B<sub>4</sub>C****(iii) Interstitial carbide : MC (Transition element or inner transitional elements forms this kind of carbide)**  
 Interstitial carbide formation doesn't affect the metallic lusture and electrical conductivity. (Q no chemical bond is present, no change in property)**(2) Hydrides :****(i) Carbon form large number of hydrides eq. Alkanes, Alkenes.****(ii) Hydrides of Si are silanes with formula Si<sub>n</sub>H<sub>2n+2</sub>. These are also called as Silicon alkanes.****(iii) Silanes with 'n' up to 8 are known.****(iv) Hydrides of Ge are called Germaines.**



- (v) Tin has only two hydrides i.e.  
 (a) Stannane –  $\text{SnH}_4$   
 (b) Distannane –  $\text{Sn}_2\text{H}_6$
- (vi) Lead has only one hydride i.e.  
 Plumbane –  $\text{PbH}_4$
- (vii) Thermal stability of hydrides ↓ Decreases, Because ( $\Delta \text{E.N}$  decreases)

**(3) Oxides :**

Carbon reacts with oxygen to form three types of oxides-

- (a) Carbon monoxide  $\text{CO}$                       (b) Carbon dioxide  $\text{CO}_2$                       (c) Carbon suboxide  $\text{C}_3\text{O}_2$

**(a) Carbon monoxide  $\text{CO}$**

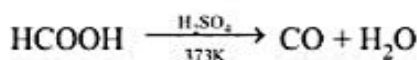
- (i) By incomplete combustion of carbon



- (ii) Reduction of oxides of heavy metals with carbon

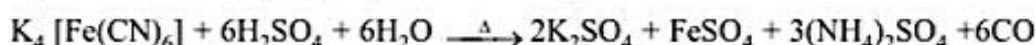


- (iii) By dehydration of formic acid with conc.  $\text{H}_2\text{SO}_4$   
 (laboratory method)



Formic acid                      (pure)

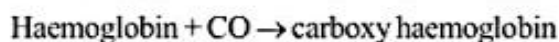
- (iv) By action of conc.  $\text{H}_2\text{SO}_4$  on potassium ferrocyanide



pot. ferrocyanide

**Physical Properties :**

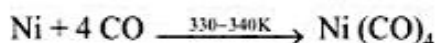
- (i) It is a neutral oxide.  
 (ii) Colourless & odourless gas, slightly soluble in water.  
 (iii) Poisonous nature due to its ability to form a stable complex with the haemoglobin present in the red blood cells.



Due to formation of stable complex with CO, Haemoglobin loses its  $\text{O}_2$  carrying capacity which causes death.

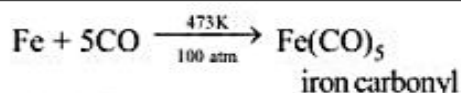
**Chemical properties**

- (i) Formation of metal carbonyls



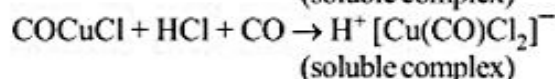
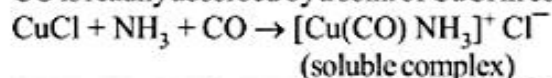
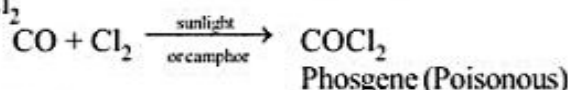
Nickel carbonyl



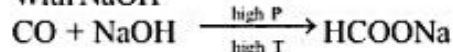


## (ii) Absorption

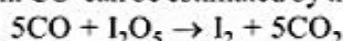
CO is readily absorbed by a soln. of CuCl in conc. HCl or NH<sub>3</sub> due to the formation of soluble complexes

(iii) With Cl<sub>2</sub>

## (iv) With NaOH

**Estimation of carbon monoxide :**

- (i) It reduces iodine pentoxide to iodine & this iodine can be titrated with standard sodium thio sulphate solution. CO can be estimated by this method.



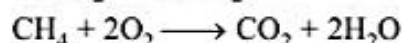
- (ii) CO does not support combustion but itself burns in air with a blue flame producing carbonsuboxide.

**Tests of carbon monoxide :**

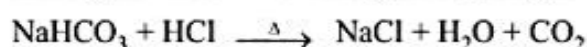
- (i) It burns with blue flame.  
 (ii) Filter paper soaked with PdCl<sub>2</sub> is turned pink, green or black. PdCl<sub>2</sub> is reduced to the metal.  
 (iii) It reduces iodine penta oxide into free iodine, which give colour with CCl<sub>4</sub>, CS<sub>2</sub> or CHCl<sub>3</sub>.

**(b) Carbon dioxide CO<sub>2</sub>****Preparation**

- (i) By burning carbon, fossil fuels & other org. Compounds in air



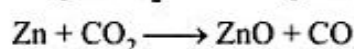
- (ii) By action of HCl on carbonates (laboratory method)

**Physical Properties :**

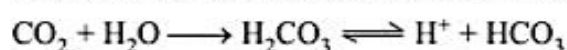
- (i) Colourless & odourless gas (about 1.5 time heavier than air)  
 (ii) Not poisonous, but does not support life.

**Chemical properties**

- (i) Non combustible nature (certain active metals Na, K, Mg burn in it)



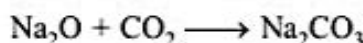
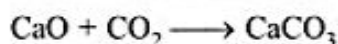
- (ii) Acidic nature : It dissolves in water to some extent to form carbonic acid.



carbonic acid

(weak dibasic acid)  $2\text{H}^+ + \text{CO}_3^{2-}$

it reacts with metallic oxides

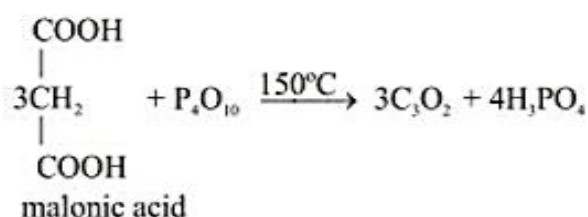


(c) **Carbon suboxide**  $\text{C}_3\text{O}_2$

(i) Structure:  $\text{O} = \text{C} = \text{C} = \text{O}$  (Linear)

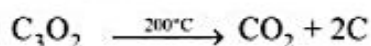
**Preparation :**

By heating malonic acid with phosphorus penta oxide



**Properties :**

- (i) Colourless gas, B.P.  $60^\circ\text{C}$
- (ii) Very readily polymerises to give coloured salts.
- (iii) It decomposes at  $2000^\circ\text{C}$

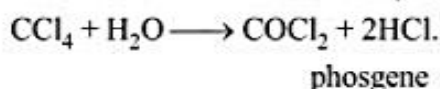


(4) **Oxyacids :**

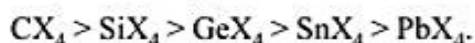
- (i) Oxyacids are formed by C & Si.
- (ii) Main inorganic oxyacid is  $\text{H}_2\text{CO}_3$
- (iii)  $\text{H}_2\text{SiO}_3$  is silica acid.

(5) **Halides :**

- (i) They form tetra halides  $\text{MX}_4$  except  $\text{PbBr}_4$  &  $\text{PbI}_4$ .
- (ii) The non existence of  $\text{PbBr}_4$  and  $\text{PbI}_4$  is due to that  $\text{Pb}^{+4}$  is a strong oxidising agent while  $\text{Br}^-$  &  $\text{I}^-$  are highly reducing agent.
- (iii) All  $\text{MX}_4$  are covalent except  $\text{SnF}_4$ . It is Ionic.
- (iv) The tetrahalides of carbon cannot undergo hydrolysis due to non availability of vacant 'd' orbitals



- (v) The tetrahalides of silicon like  $\text{SiF}_4$  can form  $\text{SiF}_6^{2-}$ . In this ion silicon undergoes  $\text{sp}^3\text{d}^2$  hybridisation where carbon cannot form this type of ion.
- (vi) Dihalides of these elements are more ionic than their corresponding tetrahalides.
- (vii) Thermal stability of tetrahalides



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**Illustration**


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1. Which element-element bond has the highest bond dissociation energy?

(A) C—C (B) Si—Si (C) Ge—Ge (D) Sn—Sn

Ans. (A)

Sol. C—C bond dissociation energy is 355 kJ mol<sup>-1</sup> which is highest amongst the carbon family members.

2. In graphite, electrons are

(A) Localised on every third C-atom (B) Present in anti-bonding orbital  
(C) Localised on each C-atom (D) Spread out between the structure.

Ans. (D)

Sol. In graphite, each carbon is sp<sup>2</sup>-hybridized and forms four covalent bonds with other C-atoms overlap side wise to give  $\pi$ -electron cloud which is delocalized and thus the electrons are spread out between the structure.

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**Exercise**


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1. Consider following statements :

I : In diamond, each carbon atom is linked tetrahedrally to four other carbon atoms by sp<sup>3</sup> bonds.

II : Graphite has planar hexagonal layers of carbon atoms held together by weak vander Waals forces

III : Silicon exists only in diamond structure due to its tendency to form p<sub>p</sub>—p<sub>p</sub> bonds to itself.

In this :

(A) Only I and II are correct (B) Only I is correct  
(C) Only II and III are correct (D) All are correct statements

Ans. (D)

2. Select correct statement :

(A) Oxides of carbon family (MO<sub>2</sub>) are all network solids with octahedral coordination

(B) Silicon dioxide (silica) is a network solid with tetrahedral coordination and is a giant molecule

(C) GeO<sub>2</sub>, SnO<sub>2</sub> and PbO<sub>2</sub> are all network solids with octahedral coordination

(D) None appears correct

Ans. (B), (C)

---

### SILICON (Si)

**Occurrence**

Silicon is the second most abundant (27.2%) element after oxygen (45.5%) in the earth's crust. It does not occur free in nature but in the combined state, it occurs widely in form of silica and silicates. All mineral rocks, clays and soils are built of silicates of magnesium, aluminium, potassium or iron. Aluminium silicate is however the most common constituent of rocks and clays.

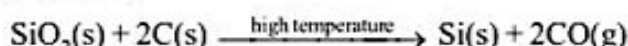
Silica is found in the free state in sand, flint and quartz and in the combined state as silicates like

- (i) Feldspar — K<sub>2</sub>O. Al<sub>2</sub>O<sub>3</sub>. 6SiO<sub>2</sub>
  - (ii) Kaolinite — Al<sub>2</sub>O<sub>3</sub>. 2SiO<sub>2</sub>. 2H<sub>2</sub>O
  - (iii) Asbestos — CaO. 3MgO. 4SiO<sub>2</sub>
-

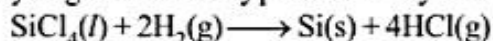


**Preparation**

- (i) From silica (sand): Elemental silicon is obtained by the reduction of silica ( $\text{SiO}_2$ ) with high purity coke in an electric furnace.



- (ii) From silicon tetrachloride ( $\text{SiCl}_4$ ) or silicon chloroform ( $\text{SiHCl}_3$ ): Silicon of very high purity required for making semiconductors is obtained by reduction of highly purified silicon tetrachloride or silicon chloroform with dihydrogen followed by purification by zone refining.

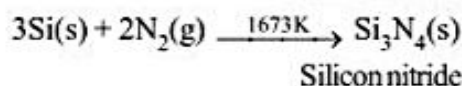
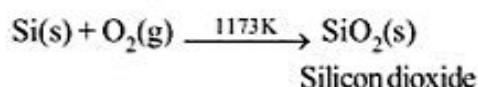
**Physical Properties :**

- (i) Elemental silicon is very hard having diamond like structure.  
 (ii) It has shining luster with a melting point of 1793 K and boiling point of about 3550 K.  
 (iii) Silicon exists in three isotopes, i.e.  $^{28}_{14}\text{Si}$ ,  $^{29}_{14}\text{Si}$  and  $^{30}_{14}\text{Si}$  but  $^{28}_{14}\text{Si}$  is the most common isotope.

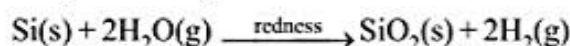
**Chemical Properties:**

Silicon is particularly unreactive at room temperature towards most of the elements except fluorine. Some important chemical reactions of silicon are discussed below.

- (i) **Action of air :** Silicon reacts with oxygen of air at 1173 K to form silicon dioxide and with nitrogen of air at 1673 K to form silicon nitride,.



- (ii) **Action of steam :** It is slowly attacked by steam when heated to redness liberating dihydrogen gas.

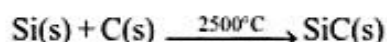


- (iii) **Reaction with halogens:** It burns spontaneously in fluorine gas at room temperature to form silicon tetrafluoride ( $\text{SiF}_4$ ).



However, with other halogens, it combines at high temperatures forming tetrahalides.

- (iv) **Reaction with carbon :** Silicon combines with carbon at 2500 °C forming silicon carbide ( $\text{SiC}$ ) known as carborundum.



Carborundum is an extremely hard substance next only to diamond. It is mainly used as an abrasive and as a refractory material.

**USES:**

- (i) Silicon is added to steel as such or more usually in form of ferrosilicon (an alloy of Fe and Si) to make it acid-resistant.  
 (ii) High purity silicon is used as semiconductors in electronic devices such as transistors.  
 (iii) It is used in the preparation of alloys such as silicon-bronze, magnesium silicon bronze and ferrosilicon.

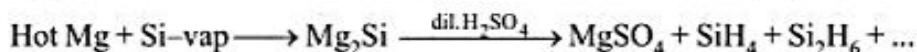


**Compounds of Silicon :****(1) Hydride**

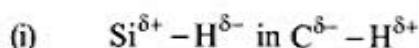
Silane  $\text{Si}_n\text{H}_{2n+2}$  ( $\text{SiH}_4$  &  $\text{Si}_2\text{H}_6$ )

Only these two are found

Higher molecules are not formed.  $\therefore$  Si can't show catanation property



**Ques.**  $\text{SiH}_4$  is more reactive than  $\text{CH}_4$ . Explain

Reasons

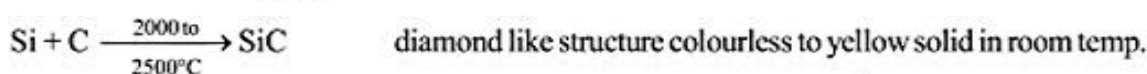
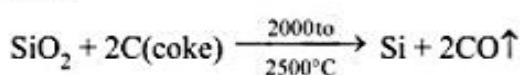
C - electro-ve than H

Si less electro-ve than H

So bond polarity is reversed when  $\text{Nu}^-$  attacks, it faces repulsion in C but not in Si

(ii) Silicon is having vacant d orbital which is not in case of carbon

(iii) Silicon is larger in size compared to C. By which the incoming  $\text{Nu}^-$  doesn't face any steric hindrance to attack at Si whereas  $\text{CH}_4$  is tightly held from all sides.

**(2) SiC (Carborundum)****Preparation**

when impurity is present

**Properties**

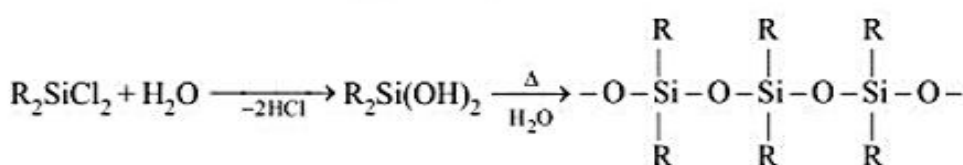
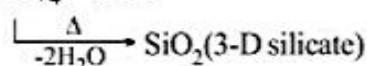
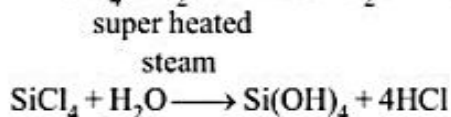
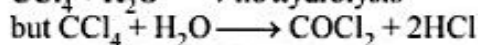
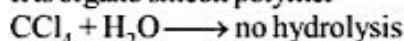
(i) It is very hard and is used in cutting tools and abrasive powder (polishing material)

(ii) It is very much inert

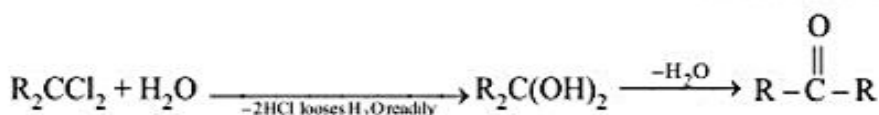
(iii) It is not being affected by any acid except  $\text{H}_3\text{PO}_4$

**(3) Silicones**

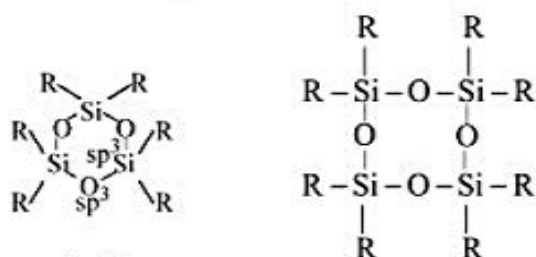
It is organo silicon polymer



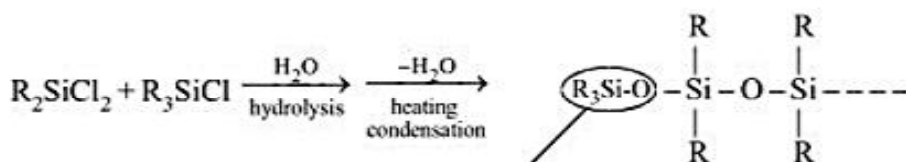
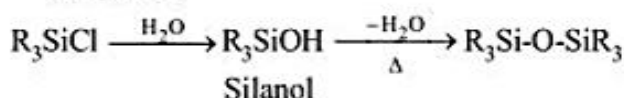
**Linear silicone**



Silicones may have the cyclic structure also having 3, 4, 5 and 6 nos. of silicon atoms within the ring. Alcohol analogue of silicon is known as silanol

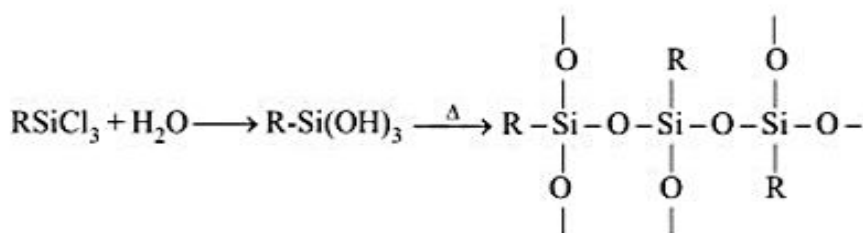


cyclic silicone  
not planar



This end of the chain can't be extended hence  
 $\text{R}_3\text{SiCl}$  is called as chain stopping unit

\* Using  $\text{R}_3\text{SiCl}$  in a certain proportion we can control the chain length of the polymer



**cross linked silicone 3 dimensional network**

It provides the crosslinking among the chain making the polymer more hard and hence controlling the proportion of  $\text{RSiCl}_3$  we can control the hardness of polymer.

#### Uses

- (1) It can be used as electrical insulator (due to inertness of Si-O-Si bonds)
- (2) It is used as water repellant ( $\because$  surface is covered) eg. car polish, shoe polish, massonary works in buildings
- (3) It is used as antifoaming agent in sewage disposal, beer making and in cooking oil used to prepare potato chips.
- (4) As a lubricant in the gear boxes.

#### (4) Silica ( $\text{SiO}_2$ )

##### Occurrence:

Silica or silicon dioxide occurs in nature in the free state as sand, quartz and flint and in the combined state as silicates like, Feldspar :  $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ , Kaolinite :  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$  etc.

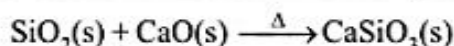
**PROPERTIES:**

- (i) Pure silica is colourless, but sand is usually coloured yellow or brown due to the presence of ferric oxide as an impurity.

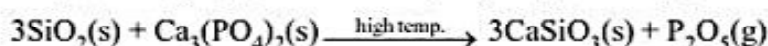
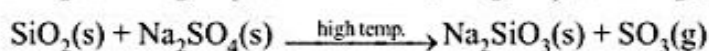
- (ii) Silicon dioxide is insoluble in water and all acids except hydrofluoric acid.  

$$\text{SiO}_2(\text{s}) + 4\text{HF}(\text{l}) \longrightarrow \text{SiF}_4(\text{l}) + 2\text{H}_2\text{O}(\text{l})$$

- (iii) It also combines with metallic oxides at high temperature giving silicates e.g.



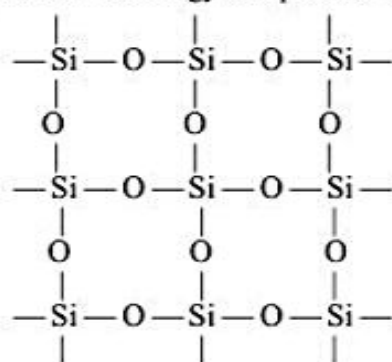
- (iv) When silica is heated strongly with metallic salts, silicates are formed and the volatile oxides are driven off as vapours.



The first two examples quoted here are important in glass making.

**Structures of Silica :**

Silica has a three-dimensional network structure. In silica, silicon is  $\text{sp}^3$ -hybridized and is thus linked to four oxygen atoms and each oxygen atom is linked to two silicon atoms forming a three-dimensional giant molecule as shown in figure. This three-dimensional network structure imparts stability to  $\text{SiO}_2$  crystal and hence a large amount of energy is required to break the crystal resulting in high melting point.

**Uses :**

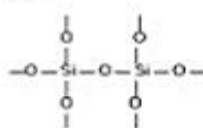
- (i) Sand is used in large quantities to make mortar and cement.
- (ii) Being transparent to ultraviolet light, large crystal of quartz are used for making lenses for optical instruments and for controlling the frequency of radio-transmitters.
- (iii) Powdered quartz is used for making silica bricks.
- (iv) Silica gel ( $\text{SiO}_2 \cdot x\text{H}_2\text{O}$ ) is used as a desiccant (for absorbing moisture) and as an adsorbent in chromatography.

### Illustration

1. In silicon dioxide  
 (A) Each silicon atom is surrounded by four oxygen atoms and each oxygen atom is bonded to two silicon atoms  
 (B) Each silicon atom is surrounded by two oxygen atoms and each oxygen atom is bonded to two silicon atoms  
 (C) Silicon atom is bonded to two oxygen atoms  
 (D) There are double bonds between silicon and oxygen atoms

Ans. (A)

Sol.

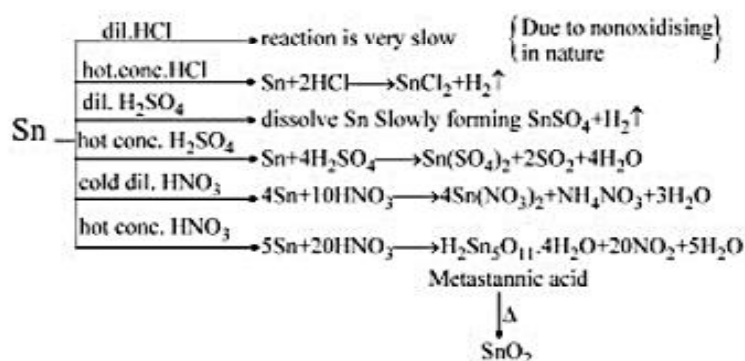
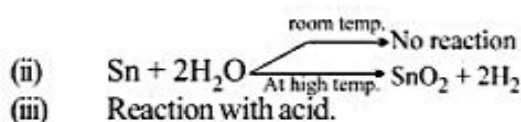
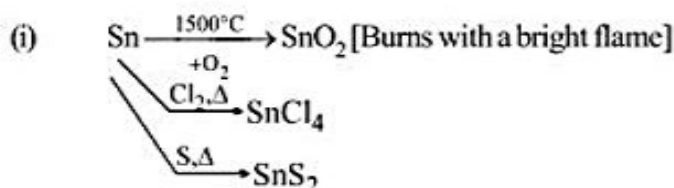


### Exercise

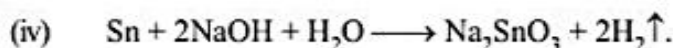
1. Which is/are true statement(s) about silicones ?  
 (A) They are repeating units ( $\text{SiO}_4$ ) in silicates  
 (B) They are synthetic polymers containing repeated  $\text{R}_2\text{SiO}_2$  units  
 (C) They are formed by hydrolysis of  $\text{R}_2\text{SiCl}_2$  units  
 (D) None is correct

Ans. (B), (C)

### TIN & ITS COMPOUND







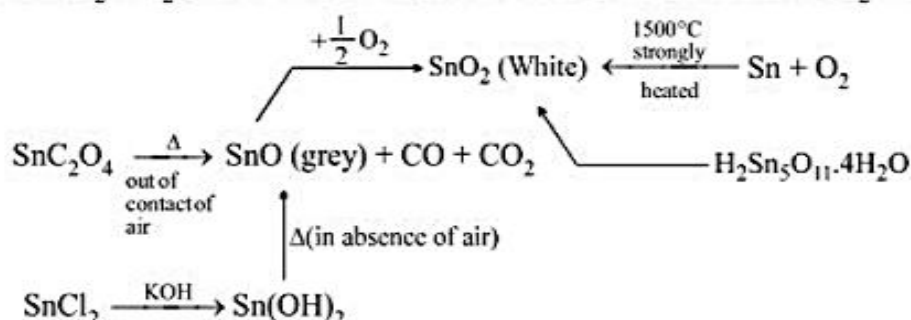
or

$\text{KOH}$  [In absence of air  $\text{Na}_2\text{SnO}_2$  forms and in contact with air it readily converts into  $\text{Na}_2\text{SnO}_3$ ]

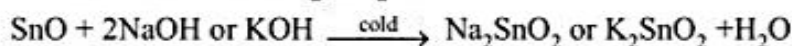
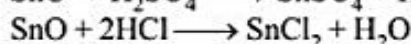
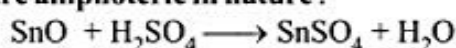
**Oxides:**

**$\text{SnO}$  (grey)**

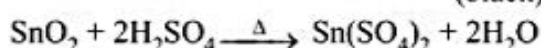
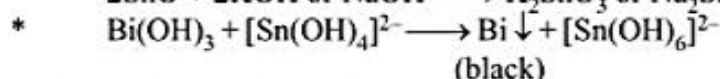
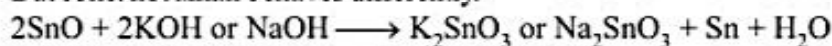
**&  $\text{SnO}_2$  (white)**



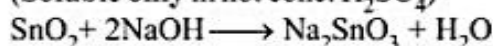
**Both are amphoteric in nature :**



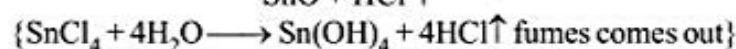
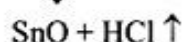
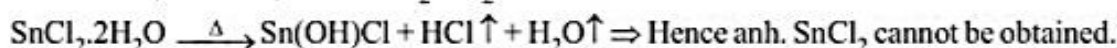
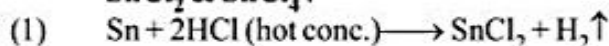
But conc. hot alkali behaves differently.



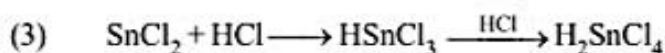
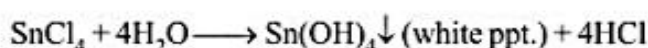
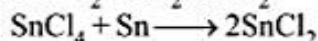
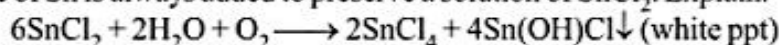
(Soluble only in hot conc.  $\text{H}_2\text{SO}_4$ )



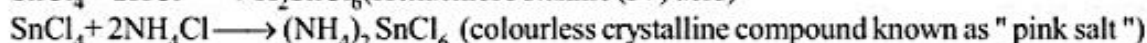
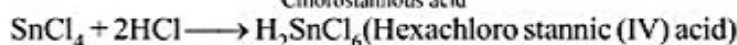
**$\text{SnCl}_2$  &  $\text{SnCl}_4$  :**



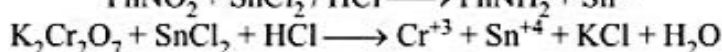
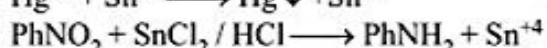
(2) A piece of Sn is always added to preserve a solution of  $\text{SnCl}_2$ . Explain.



Chlorostannous acid



(4) **Red Prop. of  $\text{SnCl}_2$  :**



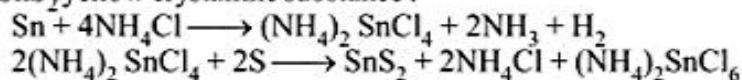
- (5) Readily combines with  $I_2 \Rightarrow SnCl_2I_2 \Rightarrow$  This reaction is used to estimate tin.

**Formation of  $SnCl_4$ :**

- (i)  $Sn + Cl_2 \xrightarrow[\text{(dry)}]{\text{(Excess)}}$   $SnCl_4$  (molten) (ii)  $2HgCl_2 + SnCl_2 \longrightarrow 2Hg \downarrow + SnCl_4$   
 (iii)  $Sn + Aq. \text{ rigia} \longrightarrow SnCl_4 + NO + H_2O$

- \*  $SnCl_4 \cdot 5H_2O$  is known as butter of tin  $\Rightarrow$  used as mordant.  
 $(NH_4)_2 SnCl_6$  is known as 'pink salt'  $\Rightarrow$  used as calico printing.

**Mosaic gold:**  $SnS_2$  yellow crystalline substance:



- \* **Distinction of  $Sn^{+2} / Sn^{+4}$ :**

- (i)  $H_2S$  (ii)  $Hg^{+2}$  (iii)  $Fe^{+3} + K_3[Fe(CN)_6] \xrightarrow{Sn^{+2}} \text{Blue ppt.}$

**Illustration**

1. Which of the following statements is not true -  
 (A)  $SnCl_2$  is ionic solid (B)  $SnCl_4$  is reducing in nature  
 (C)  $SnCl_2$  is reducing in nature (D)  $SnCl_4$  is covalent liquid

**Ans. (B)**

**Sol.**  $Sn^{+4}$  is more stable than  $Sn^{+2}$

**Exercise**

1. When tin is boiled with alkali solution, the product is -  
 (A)  $SnO_2$  (B)  $Sn(OH)_2$  (C)  $Sn(OH)_4$  (D\*)  $SnO_3^{2-}$   
**Ans. (D)**

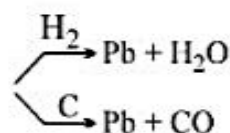
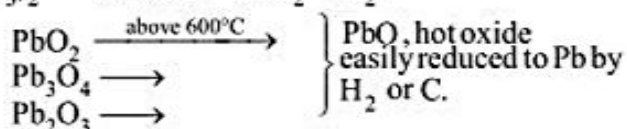
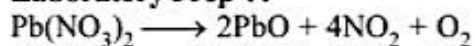
**COMPOUNDS OF LEAD**

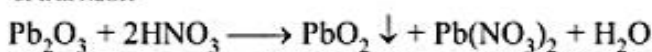
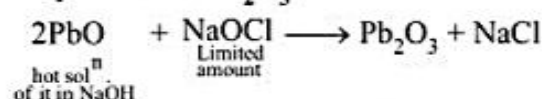
**Oxides of lead:**

- (i)  $PbO$  (ii)  $Pb_3O_4$  (Red)  
 (iii)  $Pb_2O_3$  (reddish yellow) (Sesquioxide) (iv)  $PbO_2$  (dark brown)

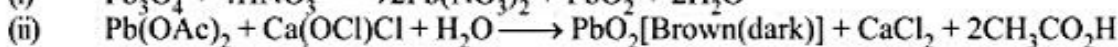
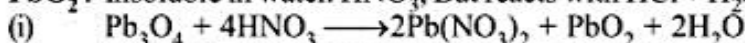
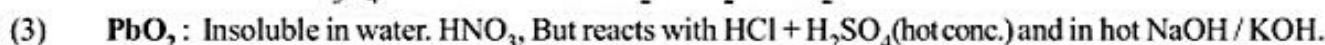
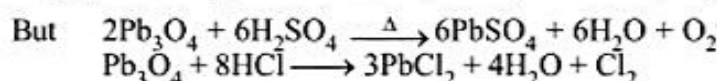
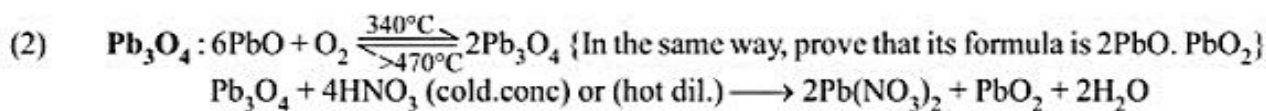
- (1)  $PbO \begin{cases} \rightarrow \text{Yellow (Massicot)} \\ \rightarrow \text{Reddish yellow (litharge)} \end{cases} \xrightarrow[\text{and powdered}]{\text{fused, cooled}} \text{Litharge}$

**Laboratory Prep<sup>n</sup>:**

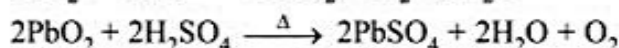


**Preparation of  $\text{Pb}_2\text{O}_3$  :**

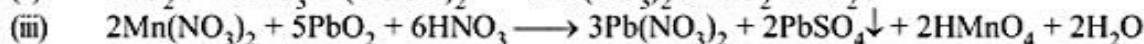
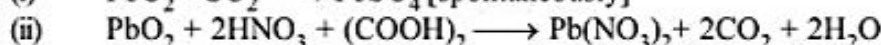
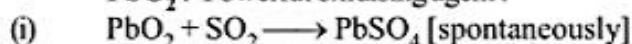
This reaction suggests that  $\text{Pb}_2\text{O}_3$  contains  $\text{PbO}_2$ .



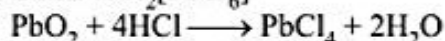
Excess bleaching powder  
is being removed by stirring with  
 $\text{HNO}_3$



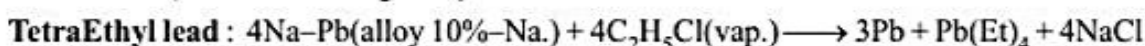
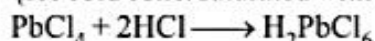
$\text{PbO}_2$  : Powerful oxidising agent :



$\text{PbCl}_4$  : Exists as  $\text{H}_2[\text{PbCl}_6]$



{ice cold conc. saturated with  $\text{Cl}_2$ }



It is antiknocking agent.

**Illustration**

1.  $\text{PbF}_4$ ,  $\text{PbCl}_4$  exist but  $\text{PbBr}_4$  and  $\text{PbI}_4$  do not exist because of -

- (A) Large size of  $\text{Br}^-$  and  $\text{I}^-$  (B) Strong oxidising character of  $\text{Pb}^{4+}$   
 (C) Strong reducing character of  $\text{Pb}^{4+}$  (D) Low electronegativity of  $\text{Br}^-$  and  $\text{I}^-$

**Ans.** (C)

**Sol.** Due to the inert pair effect  $\text{Pb}^{+2}$  is more stable than  $\text{Pb}^{+4}$  but F & Cl act as a oxidant so  $\text{PbF}_4$  &  $\text{PbCl}_4$  exist. I & Br act as a reducing agent so  $\text{PbBr}_4$  and  $\text{PbI}_4$  do not exist.

**Exercise**

1. Sindoor used by women is an oxide of lead with the formula -

- (A)  $\text{PbO}$  (B)  $\text{PbO}_2$  (C)  $\text{Pb}_3\text{O}_4$  (D)  $\text{Pb}_2\text{O}_3$

**Ans.** (C)



## SOLVED EXAMPLE

**Q.1** Choose the correct order of extent of polymerization is

- (A)  $\text{SiO}_4^{4-} > \text{PO}_4^{3-} > \text{ClO}_4^- > \text{SO}_4^{2-}$  (B)  $\text{PO}_4^{3-} > \text{ClO}_4^- > \text{SO}_4^{2-} > \text{SiO}_4^{4-}$   
 (C)  $\text{SiO}_4^{4-} > \text{SO}_4^{2-} > \text{ClO}_4^- > \text{PO}_4^{3-}$  (D)  $\text{SiO}_4^{4-} > \text{PO}_4^{3-} > \text{SO}_4^{2-} > \text{ClO}_4^-$

**Ans.** (D)

**Sol.** A extent of double bond formation of M–O bond increases due to which extent of polymerization reduces.

**Q.2** Group 13 elements exhibit

- (A) Only +3 oxidation state (B) Only +1 oxidation state  
 (C) Both +1 and +3 oxidation states (D) +1, +2 and +3 oxidation states.

**Ans.** (C)

**Sol.** As there are electrons in the valence shell of group 13 elements they show +3 oxidation state. Also in case of heavier members, due to inert pair effect, +1 oxidation state is most stable.

**Q.3** Boron compounds behave as Lewis acids because of their

- (A) Acidic nature (B) Covalent nature  
 (C) Electron deficient character (D) Ionization property

**Ans.** (C)

**Sol.** Boron compounds are electron deficient and therefore, behave as Lewis acids.

**Q.4** Moissan boron is

- (A) Amorphous boron of ultra purity (B) Crystalline boron of ultra purity  
 (C) Amorphous boron of low purity (D) Crystalline boron of low purity

**Ans.** (C)

**Sol.** Moissan boron is amorphous boron, obtained by reduction of  $\text{B}_2\text{O}_3$  with Na or Mg. It has 95-98% boron and is black in colour.

**Q.5** Both boron and aluminium show difference in properties from the remaining members of group 13. This is because

- (A) Both B and Al have smaller size as compared to other members of the family.  
 (B) Both B and Al have high values of ionization energy  
 (C) Both B and Al have only the valence electrons ( $ns^2 np^1$ ) outside the noble gas core while the remaining elements have filled d and f-orbitals in between the noble gas core and the valence electrons  
 (D) None of the above.

**Ans.** (C)

**Sol.** The difference in properties of B and Al from the remaining members of group 13 is due to the difference in their electronic configuration as stated.

**Q.6** Aluminothermy used for on the spot welding of large iron structures is based upon the fact that

- (A) As compared to iron, aluminium has greater affinity for oxygen  
 (B) As compared to aluminium, iron has greater affinity for oxygen  
 (C) Reaction between aluminium and oxygen is endothermic  
 (D) Reaction between iron and oxygen is endothermic

**Ans.** (A)

**Sol.** Al is more electropositive and has greater affinity for oxygen than iron. This fact is made use of in aluminothermy.



**Q.7** Aluminium chloride exists as a  
(A) Monomer (B) Dimer (C) Trimer (D) Polymer

**Ans.** (B)

**Sol.**  $\text{AlCl}_3$  is electron deficient. Al completes its octet by forming a dimer  $\text{Al}_2\text{Cl}_6$ .

**Q.8** Which property is not exhibited by carbon in its compounds ?  
(A) Forming bonds to other carbon atoms  
(B) Forming multiple bonds  
(C) Exhibiting allotropic forms  
(D) Forming compounds with coordination number beyond four.

**Ans.** (D)

**Sol.** Carbon cannot expand its coordination number beyond four due to the absence of d-orbitals.

**Q.9** A solid element (symbol Y) conducts electricity and forms two chlorides  $\text{YCl}_n$  (a colourless volatile liquid) and  $\text{YCl}_{n-2}$  (a colourless solid). To which one of the following groups of the periodic table does Y belong ?

(A) 13 (B) 14 (C) 15 (D) 16

**Ans.** (B)

**Sol.** Element Y belongs to group 14 of the periodic table which forms two chlorides  $\text{YCl}_4$  (a colourless, volatile liquid) and  $\text{YCl}_2$  (a colourless solid).

# THERMODYNAMICS

## INTRODUCTION

The study of energy transformations is the subject matter of thermodynamics. Various forms of energy are interrelated and under certain conditions, these may be transformed from one form into another. In a chemical reactions, energy stored by molecules can be released as heat. The chemical energy may also be used to do mechanical work when a fuel burns in an engine.

The laws of thermodynamics can be applied with energy changes of macroscopic systems involving a large number of molecules rather than microscopic systems containing a few molecules. Moreover thermodynamics is not concerned about how and at what rate these energy transformations are carried out, but is based on initial and final states of a system undergoing the change.

### Objectives and limitations of thermodynamics :

#### Objectives :

- (1) Interrelate various energy changes during physical or chemical transformation.
- (2) Predict the feasibility of given change.
- (3) Deduce various laws, e.g. phase rule, distribution law, law of mass action etc. thermodynamically.
- (4) Derive at what conditions, the equilibrium is attained by a change.

#### Limitations :

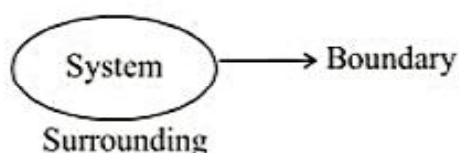
- (1) Its laws are valid for bulk of matter and does not provide information about individual atom.
- (2) It predicts feasibility of reaction but fails to suggest rate of reaction.
- (3) It fails to explain the systems which are not in equilibrium.

## SOME BASIC TERMS

### 1. System

A specified part of the universe with real or imaginary boundaries, on which studies of P, T etc are to be made.

A room, an engine human body etc. are examples of system.



### 2. Surrounding

The rest part of the universe, adjacent to real or imaginary boundaries of the system.

Universe = System + Surrounding

**Note :** For practical purpose, surrounding means immediate surrounding rather than universe. For example in Lab experiment the room is considered as surrounding.

### 3. Types of system

#### (A) Based on exchange of mass and energy

- (i) **Isolated system** : A system is said to be isolated if it cannot exchange matter and energy with the surroundings. Example : coffee in a thermos flask.
- (ii) **Closed system** : A system is said to be closed if it can exchange energy but not matter. Example: Coffee in a closed stainless steel flask.
- (iii) **Open system** : A system is said to be open if it can exchange matter. Example : A thermos flask or a steel flask if not closed.

#### (B) Based on system composition

- (i) **Homogeneous systems** : A system having uniform nature throughout, made up of one phase only
- (ii) **Heterogeneous system** : A system not uniform throughout, consists of more than one phase.

## PROPERTIES OF A SYSTEM

The state of a system is defined by a particular set of its measurable quantities called properties, by which a system can be described for example, Temperature (T), Pressure (P) and volume (V) defines the thermodynamics state of the system in the same way, as particle co-ordinate is defined by (x, y, z) co-ordinate in physics. Properties can be categorised into extensive and intensive properties, on the basis of dependance of system size or mass.

**Intensive property** is one whose value is independent of the size (or mass) of the system.

**Extensive property** is one whose value depends on the size (or mass) of the system.

### Intensive & Extensive properties

1. Extensive properties are additive but intensive properties are non additive.
2. Ratio of two extensive property gives an intensive property.
3. An extensive property can be converted into intensive property by defining it per mole/ per gram/ per litre.

Extensive Properties	Intensive Properties
Volume	Molar volume
Number of moles	Density
Mass	Refractive index
Free Energy (G)	Surface tension
Entropy (S)	Viscosity
Enthalpy (H)	Free energy per mole
Internal energy (E & U)	Specific heat
Heat capacity	Pressure
	Temperature
	Boiling point, freezing point etc



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**Exercise**


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1. Select the intensive and extensive properties from the following :  
Entropy, specific entropy, triple point of water , volume of gas, pressure

**Ans.** Intensive property : Specific entropy, triple point of water, pressure,  
Extensive property : Entropy,

---

A function may be state or path function depending on the dependence on path of the process or the end state.

- (A) **State function or State variable :** Variables like P, V , T are *State Functions* or *State Variables* because their values depend only on the present state of a system and not on how the state was reached.

**Mathematical Condition for a function to be a state function :**

There are three conditions that must be satisfied simultaneously for a function to be state function.

- (i) If  $\phi$  is a state function

$$\int_A^B d\phi = \phi_B - \phi_A$$

It means change in  $\phi$  depends only on end states and not on the path which it followed during the process.

- (ii) If  $\phi$  is a state function

$$\oint d\phi = 0$$

It implies, in cyclic integral as the end states are same, so  $\Delta\phi$  value will be zero.

- (iii) If  $\phi = f(x, y)$  is a state function, Euler's reciprocity theorem must be satisfied.

$$\frac{\partial}{\partial y} \left[ \left( \frac{\partial \phi}{\partial x} \right)_y \right]_x = \frac{\partial}{\partial x} \left[ \left( \frac{\partial \phi}{\partial y} \right)_x \right]_y$$

(B) **Path function**

Functions which depend on the path means how the process is carried out to reach a state from another state depends on path e.g. work & heat.

**State function :** Pressure, volume, temperature, Gibb's free energy, internal energy, entropy

**Path function :** Work, Heat, Loss of energy due to friction

*Note : S, U, H, V, T etc are state function but  $\Delta S, \Delta U, \Delta H, \Delta V, \Delta T$ , etc. are not state function. In fact  $\Delta$  terms are not function itself and it is very misleading and frequently asked in the exams.*

---



**Illustration**

1. Show that pressure of a fixed amount of an ideal gas is a state function  $V = \frac{nRT}{p}$

Sol.  $\left(\frac{\partial V}{\partial T}\right)_p = \frac{nR}{p}$

$$\frac{\partial}{\partial p} \left[ \left( \frac{\partial V}{\partial T} \right)_p \right]_T = \frac{-nR}{p^2} \Rightarrow \left( \frac{\partial V}{\partial p} \right)_T = -\frac{nRT}{p^2}$$

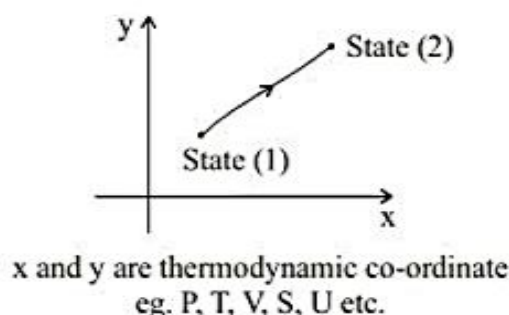
$$\Rightarrow \frac{\partial}{\partial T} \left[ \left( \frac{\partial V}{\partial p} \right)_T \right]_p = \frac{-nR}{p^2}$$

**Exercise**

1. Show that Volume of a fixed amount of an ideal gas is a state function.

**THERMODYNAMIC PROCESS**

The change of thermodynamic state from one condition to another condition is called thermodynamic process.

**(1) Reversible and Irreversible process**

A process which is carried out so slowly that the system and the surroundings are always in equilibrium during the process is known as a **Reversible Process (quasi-static)**. If this condition does not hold good, the process is said to be, **Irreversible**.

In a reversible process the driving force is infinitesimally larger than the opposing force.

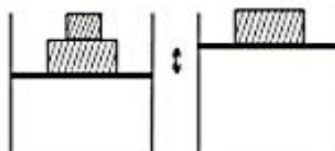
A reversible process is very slow and takes infinite time. Whereas an irreversible process completes in finite time.

**Note :**

- This thermodynamic reversible process is different from the “reversible reactions”. The term “Reversible reaction” only indicates that the reaction proceeds in both the directions.
- A process which proceeds without any external help is called a spontaneous process.
- All the real process are irreversible process



Reversible process



irreversible process

S.No.	Reversible process	Irreversible process
1.	Driving force is infinitesimally small.	Driving force is large and finite. PV
2.	PV work is done across pressure difference $dp$	work is done across pressure difference $\Delta P$
3.	A reversible heat transfer take place across temperature difference $dT$	Irreversible heat transfer take place across difference $\Delta T$
4.	It is an ideal process.	It is a real process
5.	It takes infinite time for completion of process.	It takes finite time for completion of process.
6.	It is an imaginary process and can not be realised in actual practice.	It is a natural process and occurs in particular direction under given set of conditions.
7.	Throughout the process, the system remain infinitesimally closer to state of equilibrium and exact path of process can be drawn	The system is far away from state of equilibrium and exact path of process can not be defined as different part of the system are under different conditions

**(2) Isothermal Process**

- A process in which temperature of the system does not change throughout the studies.
- $dT = 0$
- It can be achieved by using thermostatic process.

**(3) Adiabatic Process**

- A process in which exchange of heat between system and surrounding does not take place.
- $q = 0$
- It can be achieved by insulating the system boundaries for heat transfer.

**(4) Cyclic Process**

- (i) A process in which initial state of system is same after a series of operation
- (ii) For a cyclic process  $\Delta E = 0$  and  $\Delta H = 0$

**(5) Isochoric Process**

- (i) A process in which volume of the system remains constant throughout, the process.
- (ii) For an Isochoric process  $\Delta V = 0$

**(6) Isobaric process**

- (i) A process in which pressure of the system remains constant throughout the process.
- (ii) Means  $\Delta P = 0$

**(7) Equilibrium :** It is defined as when there is no change in thermodynamic property (P, V, T etc) of system with time.**TYPES OF EQUILIBRIUM**

System and surrounding equilibrium condition is considered in three broader terms :

1. **Thermal equilibrium :** Equality of temperature between system and surrounding
2. **Mechanical equilibrium :** Equality of pressure between system and surrounding
3. **Material equilibrium :** No. of moles of every substance in a definite phase remains constant with respect to time. Attained in closed vessel.

**(a) Physical or phase equilibrium :** Only physical changes are involved.

eg.  $A(s) \rightleftharpoons A(l)$

$A(s) \rightleftharpoons A(g)$

$A(l) \rightleftharpoons A(g)$

**(b) Chemical equilibrium :**  $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$   
 $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

**In thermodynamics to deal with energy change during interaction of system and surrounding understanding of work (W) heat (Q, q) and internal energy (U, E) is very important.**

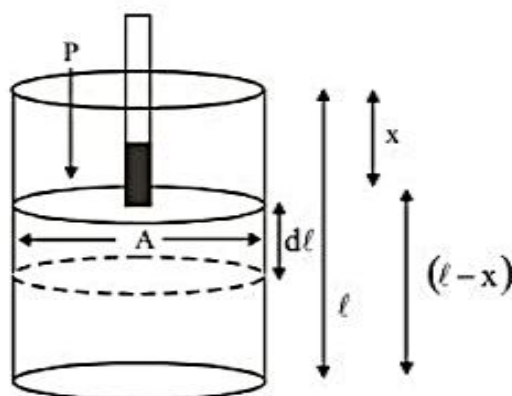
**WORK**

Energy that is transmitted from one system to another in such a way that difference of temperature is not directly involved. This definition is consistent with our understanding of work as  $dw = Fdx$ . The force F can arise from electrical, magnetic, gravitational & other sources. It is a path function.

***Note :** Litre atmosphere term is unit of energy. It is useful to remember the conversion : 1 litre atm = 101.3 Joules = 24.206 Cal.*

**PV- Work analysis :** Consider a cylinder fitted with a frictionless piston, which enclosed no more of an ideal gas. Let an external force F pushes the piston inside producing displacement in piston. Let distance of piston from a fixed point is x and distance of bottom of piston at the same fixed point is  $\ell$ . This means the volume of cylinder =  $(\ell - x)A$  where A is area of cross section of piston.





For a small displacement  $dx$  due to force  $F$ , work done on the system.

$$dw = F \cdot dx$$

Also  $F = PA$

$$dW = PA \cdot dx$$

$$V = (\ell - x)A$$

$$\Rightarrow dV = -A \cdot dx \quad \Rightarrow dW = -P_{\text{ext.}} dV$$

$$\Rightarrow W_{PV} = - \int_{V_i}^{V_f} P_{\text{ext.}} dV$$

**Note :** During expansion  $dV$  is positive and hence sign of  $w$  is negative since work is done by the system and negative sign representing decrease in energy content of system. During compression, the sign of  $dV$  is negative which gives positive value of  $w$  representing the increase in energy content of system during compression.

### Illustration

- Find the work done when 18 ml of water is getting vapourised at 373 K in open vessel (Assume the ideal behaviour of water vapour.)

**Sol.**  $PV = nRT$  [V in litre and T in Kelvin]  
 $PV = 1 \times 0.0821 \times 373$   
 $PV = 30 \text{ litre}$   
 $V = 30 \text{ litre}$   
 $W = -P\Delta V$   
 $= -1 (30 - V_{\text{gas}})$  [18 ml is negligible as compared to 30 litre]  
 $= -1 \times 30 = -30 \text{ litre atm.}$

- Calculate work done for the expansion of a substance from  $3\text{m}^3$  to  $5\text{m}^3$  against. Constant pressure =  $10^5\text{Pa}$

**Sol.**  $W = -10^5 \times 2 = -2 \times 10^5 \text{ J}$



---

**Exercise**


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1. Find the work done in each case :

- (a) When one mole of ideal gas in 10 litre container at 1 atm, is allowed to enter a vacuated bulb of capacity 100 litre.
- (b) When 1 mole of gas expands from 1 litre to 5 litre against constant atmospheric pressure.

Ans. (a)  $W = -P\Delta V$

But since gas enters the vacuum bulb and pressure in vacuums zero. This type of expansion is called free expansion and work done is zero.

**Note :-** Work done in free expansion is always zero.

- (b)  $W = -P\Delta V = -1 (5 - 1) = -4$  litre-atm.
- 

## HEAT

Heat is defined as the energy that flow into or out of a system because of a difference in temperature between the thermodynamic system and its surrounding.

According to IUPAC convention heat given by system is expressed with -ve sign heat given to system is expressed with +ve sign.

- (i)  $q_v = nC_v dT$  (for constant volume process)
- (ii)  $q_p = nC_p dT$  (for constant pressure process)
- (iii)  $C_{p,m} - C_{v,m} = R$
- (iv)  $C_v$  &  $C_p$  depends on temperature even for an ideal gas. ( $C = a + bT + cT^2$  .....
- (v) It is a path function

$C_v$ ,  $C_p$  are heat capacity of system and  $C_{v,m}$ ,  $C_{p,m}$  are heat capacity of one mole system at constant volume and pressure respectively.

## INTERNAL ENERGY (E & U)

Every system having some quantity of matter is associated with a definite amount of energy, called internal energy. Internal energy is stored in different forms inside the molecule.

$$U = U_{\text{Kinetic}} + U_{\text{Potential}} + U_{\text{Electronic}} + U_{\text{nuclear}} + \dots$$

**Note :**

1. U is a state function & is an extensive property.  

$$\Delta U = U_{\text{final}} - U_{\text{initial}}$$
  2. It does not include kinetic energy of motion of system as a whole or its potential energy due to its position.
  3.  $\Delta E = q_v$ , heat supplied to a gas at constant volume, since all the heat supplied goes to increase the internal energy of the gas.
-

4. For a given system, if  $U$  is a function of  $T$  and Volume :

$$U = f(T, V)$$

$$dU = \left( \frac{\partial U}{\partial T} \right)_V \cdot dT + \left( \frac{\partial U}{\partial V} \right)_T dV$$

5. For isochoric process :  $dV = 0$

$$dU = \left( \frac{\partial U}{\partial T} \right)_V dT$$

$$dU = C_V \cdot dT$$

$$\Delta U = \int C_V \cdot dT$$

6. For an ideal gas, change in internal energy with change in volume at constant temperature is zero.  
i.e.

$$\left( \frac{\partial U}{\partial V} \right)_T = 0$$

$$dU = C_V \cdot dT$$

$$\Delta U = \int C_V \cdot dT$$

**Internal energy is stored in the molecular motion and capacity to store energy depends upon degree of freedom of molecules**

## DEGREE OF FREEDOM AND EQUIPARTITION PRINCIPLE

According to Law of equipartition of energy

- (i) each translation and rotational degree of freedom in a molecule contributes  $1/2 RT$  to the thermal energy of one mole of a gas, and
- (ii) each vibrational degree of freedom in a molecule contributes  $RT$  to the thermal energy of one mole of a gas.

**The degree of freedom** in a molecule are given by the **number of coordinates** required to locate all the mass points (atoms) in a molecule. If a molecule contains only one atom (as in a monatomic gas), it has three degree of freedom corresponding to translational motion in the three independent spatial directions X, Y and Z. If a molecule contain  $N$  atoms, each atom contributes these three degree of freedom, so the molecule has a total of  $3N$  degree of freedom. Since three coordinates (degree of freedom) are required to represent the translational motion of the molecule, the remaining  $(3N - 3)$  coordinates represent what are called the **internal degree of freedom**. If the molecules is linear, it has two rotational degrees of freedom ; for a non-linear molecule, there are three rotational degree of freedom. The remaining degrees of freedom, that is  $3N - 5$  for linear and  $3N - 6$  for non-linear molecules are the vibrational degree of freedom. Table list the degrees of freedom for several molecular system.

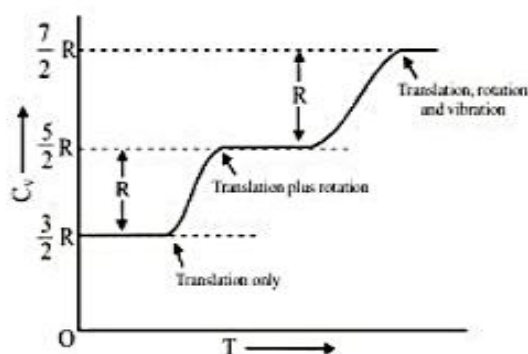
Atomicity	$n_t$	$n_{R_0}$	$n_{vib}$	$C_V$		$C_P$		$\gamma$	
				Excl. Vib	Incl. Vib	Excl. Vib	Incl. Vib	Excl. Vib	Incl. Vib
Mono	3	0	0	$\frac{3}{2}R$	$\frac{3}{2}R$	$\frac{5}{2}R$	$\frac{5}{2}R$	$\frac{5}{3}$	$\frac{5}{3}$
Di	3	2	1	$\frac{5}{2}R$	$\frac{7}{2}R$	$\frac{7}{2}R$	$\frac{9}{2}R$	$\frac{7}{5}$	$\frac{9}{7}$
Tri	Linear	3	2	$\frac{5}{2}R$	$\frac{13}{2}R$	$\frac{7}{2}R$	$\frac{15}{2}R$	$\frac{7}{5}$	$\frac{15}{13}$
	Non Linear	3	3	$3R$	$6R$	$4R$	$7R$	$\frac{4}{3}$	$\frac{7}{6}$

In a monatomic molecule  $E = 3RT/2$  is in agreement with the simple model. For a diatomic molecule, there are three translational, two rotational (because the molecule is linear) and One vibrational degree of freedom making a total of six. The thermal energy per mole.

$$\bar{E} = \left( \frac{1}{2}RT \right)_{\text{trans}} + \left( \frac{1}{2}RT \right)_{\text{rot}} + (1RT)_{\text{vib}}$$

and  $\bar{C}_V = 3R/2 + R + R = 7R/2 = 7 \text{ cal deg}^{-1} \text{ mol}^{-1}$

Table shows that the observed of  $\bar{C}_V$  for diatomic deviate greatly from the predicted values. The fact that the observed values of  $5 \text{ cal deg}^{-1} \text{ mol}^{-1}$  (which is close to  $5R/2$ ) is most common for simple diatomic molecules shows that vibration degree of freedom are active only at very high temperature. The following graph shows.



Variation of heat capacity at constant volume of a diatomic gas due to excitation of rotational and vibrational levels.

**Note :** Variation of  $C_V$  with temperature highlights the fact that with increase in the temperature the vibration modes of motion also contribute to the heat capacity

\* **Adiabatic exponent :** Adiabatic exponent ( $\gamma$ ) for a mixture of gas with different heat capacity is defined as :

$$\gamma_{\text{mix}} = \frac{n_1 C_{P_1} + n_2 C_{P_2} \dots}{n_1 C_{V_1} + n_2 C_{V_2} \dots}$$

where  $n_1, n_2 \dots$  are moles of different gases.



**Illustration**

1. Calculate change in internal energy of 10 gm of  $H_2$ , when it's state is changed from (300K, 1 Atm) to (500 K, 2 Atm)

**Sol.** For ideal gas

$$\Delta U = nC_v (T_2 - T_1) = \left(\frac{10}{2}\right) \left(\frac{5}{2} R\right) (500 - 300) = 2500 R = 5 \text{ Kcal}$$

$C_v$  for  $H_2$  (diatomic) in low temperature range will be  $5R$  as vibrational part is not included.

2. Calculate change in internal energy for a gas under going from state-I (300 K,  $2 \times 10^{-2} \text{ m}^3$ ) to state-II (400 K,  $4 \times 10^{-2} \text{ m}^3$ ) for one mol. of vanderwaal gas. [ $C_v = 12 \text{ J/K/mol}$ ]

$$\left\{ \text{Given: } \left( \frac{\partial U}{\partial V} \right)_T = T \left( \frac{\partial P}{\partial T} \right)_V - P \right.$$

$$C_v = 12 \text{ J/k/mol}$$

$$a = 2 \text{ J.m./mol}^2 \left. \right\}$$

**Sol.**  $\Delta U = C_v (T_2 - T_1) + a \left( \frac{1}{V_1} - \frac{1}{V_2} \right) = C_v (100) + a \left( \frac{1}{4} \right) \times 10^2 = 12 \times 100 + 2 \left( \frac{1}{4} \right) \times 100 = 1250$

**Exercise**

1. Calculate change in internal energy of  $CO_2$  for two mole, if temperature change is 100 K in very high temperature range.

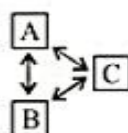
**Ans.**  $2 \times 100 \times \frac{13R}{2} = 1300 R$

( $CO_2$  is triatomic linear molecule)

**FIRST LAWS OF THERMODYNAMICS**

Laws of thermodynamic are deduced from experimental observation with logical reasons. There are four laws :

1. **Zeroth law of thermodynamics :** It is bases on thermal equation two system in thermal equation with a 3rd system are also in thermal equation with each other.





## 2. First law of Thermodynamics

"Total energy of universe remain constant." It is law of conservation of energy.

Let us consider a system whose internal energy is  $U_1$ . If the system is supplied with heat  $q$ , the internal energy of the system increases to  $U_1 + q$ . If work ( $w$ ) is now done on the system, the internal energy in the final state of the system,  $U_2$  is given by

$$U_2 = U_1 + q + w$$

or  $U_2 - U_1 = q + w$

$$\Delta U = q + w,$$

According to IUPAC, heat, added to the system and work done on the system are assigned positive values as both these modes increase the internal energy of the system.

### Illustration

1. The pressure of a fluid is a linear function of volume ( $P = a + bV$ ) and the internal energy of the fluid is  $U = 34 + 3PV$  (S.I. units). Find  $a$ ,  $b$ ,  $w$ ,  $\Delta E$  and  $q$  for change in state from (100 Pa,  $3\text{m}^3$ ) to (400 Pa,  $6\text{m}^3$ )

Sol.  $w = - \int_{V_1}^{V_2} P dV$  ( $100 = a + 3b$ ;  $400 = a + 6b$ ;  $a = -200$  &  $b = 100$ )

$$w = - \int_{V_1}^{V_2} (a + bV) dV = - \left\{ [aV] + \left[ \frac{bV^2}{2} \right] \right\}_{V_1}^{V_2}$$

$$= - [-600 + 13.5 \times 100] = -750$$

$$\Delta U = 6300$$

### Exercise

1. One mole of an ideal gas expands from state-I (1 Atm, 20 litre) to (2 Atm, 10 litre) isothermally. Calculate,  $w$  &  $\Delta U$ .

Ans.  $\Delta U = 0$ ,  $W = -nRT \ln \left( \frac{V_2}{V_1} \right) = P_1 V_1 \ln \left( \frac{V_2}{V_1} \right) = -20 \ln 2 = -14 \text{ lit-atm}$

## ENTHALPY

Enthalpy is a measure of the total energy of a thermodynamic system. It includes the internal energy, which is the energy required to create a system, and the amount of energy required to make space for it by displacing its environment and establishing its volume and pressure.

The enthalpy of a system is defined as:

$$H = U + PV$$

so

$$dH = dU + d(PV)$$

where

H is the enthalpy of the system

U is the internal energy of the system

P is the pressure at the boundary of the system and its environment

V is the volume of the system.

Note that the U term is equivalent to the energy required to create the system, and that the PV term is equivalent to the energy that would be required to "make space" for the system if the pressure of the environment remained constant.

### Property of Enthalpy parameter

1. Enthalpy is a thermodynamic potential. It is a state function and an extensive quantity.
2. The total enthalpy, (absolute value) H, of a system cannot be measured directly. Thus, change in enthalpy,  $\Delta H$ , is a more useful quantity than its absolute value.
3. The unit of measurement for enthalpy (SI) is joule.
4. The enthalpy is the preferred expression of system energy changes in many chemical and physical measurements, because it simplifies certain descriptions of energy transfer. This is because a change in enthalpy takes account of energy transferred to the environment through the expansion of the system under study.
5. The change  $\Delta H$  is positive in endothermic reactions, and negative in exothermic processes.  $\Delta H$  of a system is equal to the sum of non-mechanical work done on it and the heat supplied to it.
6. For quasistatic processes under constant pressure,  $\Delta H$  is equal to the change in the internal energy of the system, plus the work that the system has done on its surroundings. This means that the change in enthalpy under such conditions is the heat absorbed (or released) by a chemical reaction. Chemical reactions are generally carried out at constant pressure (atmospheric pressure) so it has been found useful to define a new state function *Enthalpy* (H) as :

$$H = U + PV$$

$$\Delta H = \Delta U + \Delta(PV)$$

at constant pressure

$$\Delta H = \Delta U + P \Delta V$$

combining with first law.

$$\Delta H = q_p = \text{Heat added at constant pressure}$$

**Note :**

1. Transfer of heat at constant volume brings about a change in the internal energy of the system whereas that at constant pressure brings about a change in the enthalpy of the system.

2. For a given system

$$H = f(T, P)$$

$$dH = \left( \frac{\partial H}{\partial T} \right)_P \cdot dT + \left( \frac{\partial H}{\partial P} \right)_T dP$$

3. For isobaric process :  $dP = 0$

$$dH = \left( \frac{\partial H}{\partial T} \right)_P dT$$

$$dH = C_p \cdot dT$$

$$\Delta H = \int C_p \cdot dT$$

4. For an ideal gas, change in enthalpy at constant temperature with change in pressure is zero.

i.e.

$$\left( \frac{\partial H}{\partial P} \right)_T = 0 \Rightarrow dH = C_p \cdot dT \Rightarrow \Delta H = \int C_p \cdot dT$$

- (A) Relationship between  $\Delta H$  &  $\Delta U$  :** The difference between  $\Delta H$  &  $\Delta U$  becomes significant only when gases are involved (insignificant in solids and liquids)

$$\Delta H = \Delta U + \Delta(PV)$$

If substance is not undergoing chemical reaction or phase change.

$$\Delta H = \Delta U + nR\Delta T$$

In case of chemical reaction

$$\Delta H = \Delta U + (\Delta n_g)RT$$

- (B) Difference between enthalpy and internal energy :** Chemists routinely use  $H$  as the energy of the system, but the  $pV$  term is not stored in the system, but rather in the surroundings, such as the atmosphere. When a system, for example,  $n$  mole of a gas of volume  $V$  at pressure  $P$  and temperature  $T$ , is created or brought to its present state from absolute zero, energy must be supplied equal to its internal energy  $U$  plus  $pV$ , where  $pV$  is the work done in pushing against the ambient (atmospheric) pressure. This additional energy is, therefore, stored in the surroundings and can be recovered when the system collapses back to its initial state. In basic chemistry scientists are typically interested in experiments conducted at atmospheric pressure, and for reaction energy calculations they care about the total energy in such conditions, and therefore typically need to use  $H$ . In basic physics and thermodynamics. It may be more interesting to study the internal properties of the system and therefore the internal energy is used.



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**Illustration**


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1. 1 mole of a real gas is subjected to a process from (2 bar, 40 lit., 300K) to (4 bar, 30 lit., 400 K). If change in internal energy is 20 kJ then calculate enthalpy change for the process.

**Sol.**  $\Delta H = \Delta U + \Delta(PV)$

$$\Delta(PV) = P_2V_2 - P_1V_1 = 4 \times 30 - 2 \times 40 = 40 \text{ l-bar} = 4 \text{ kJ}$$

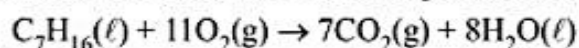
$$\Delta H = 20 + 4 = 24$$


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**Exercise**


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1. 1150 kcal heat is released when following reaction is carried out at constant volume 27°C



Find the heat change at const. pressure.

**Ans.** -1152.4 KCal

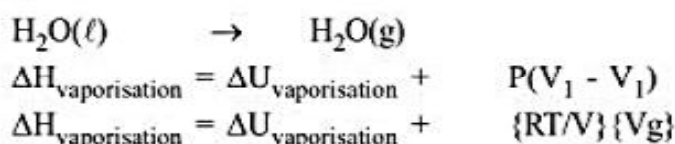
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- (C) **Change in internal energy and enthalpy in phase transition :-** At certain temperature under one atmospheric pressure, one phase change into other phase by taking certain amount of Heat. The temperature at which this happens is called transition temperature and heat absorbed during the process is called Enthalpy of phase transition. Heat absorbed during transition is exchanged at constant pressure and temperature and it is significant to know that the process is reversible.

**Fusion :-** Solid ice at 273 K and 1 atm pressure reversibly changes into liquid water. Reversibly, isothermally and isobarically, absorbed heat is known as latent heat of fusion or enthalpy of fusion.

**Vaporisation :-** Water at 373K and 1 atm pressure changes into vapors absorbed heat is known as latent heat of vaporisation. The latent heat of vaporisation is heat exchanged isothermally, isobarically and reversibly to convert water into its vapour at boiling point.

Internal energy change of phase transitions involving gas phase has no practical significance because it is not possible to carry out  $\Delta U$  of phase transition directly through an experiment. However  $\Delta U$  of phase transition can be determined theoretically from experimentally obtained value of  $\Delta H$  of phase transition.



Ignore volume of liquid as it is very less compared to gas under normal pressure.

$$\Rightarrow \Delta H_{\text{vap.}} = \Delta U_{\text{vap.}} + RT$$

where R is gas constant and T absolute temperature for condensed phase transitions for solid liquid transitions

$$\Delta H_{\text{vap.}} \simeq \Delta U_{\text{vap.}}$$


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## CALCULATION OF WORK DONE IN VARIOUS PROCESS

1. **Isothermal process :** In isothermal process, work done can be calculated as

$$w = - \int_{V_1}^{V_2} P dV$$

Since  $dT = 0 \Rightarrow dU = 0$  for an ideal gas

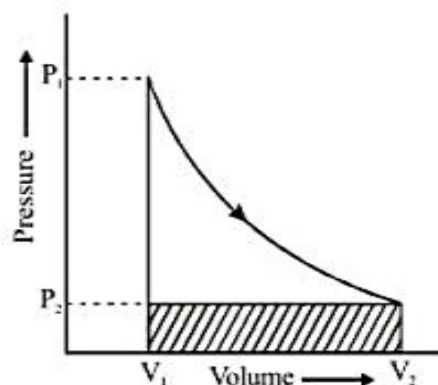
from 1<sup>st</sup> law  $q = -w$

- (A) If process is reversible

$$W = -nRT \ln \frac{V_2}{V_1}$$

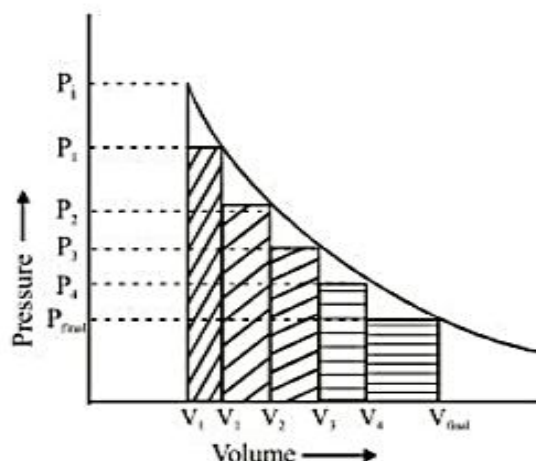
- (B) **Irreversible isothermal expansion :** If external pressure over the piston is abruptly changed from the equilibrium value, the mechanical equilibrium of system is disturbed and piston rushes out : This type of P.V work is irreversible P.V work. To calculate irreversible P.V work. Law of conservation of energy is used. Suppose as a result of difference in pressure a piston moves out and acquire kinetic energy  $\Delta KE$  and in the process volume increase by  $\Delta V$  then  $w_{irr} = -P_{ext} \Delta V - \Delta KE$ .

If after sufficient times piston come back to equilibrium state (off course in the process it moves up and down from equilibrium position many times),  $\Delta KE = 0$  : All the acquired kinetic energy is transferred back to ideal gas.



- (C) **Irreversible isothermal expansion and compression (Many steps)**

Consider an irreversible expansion of an ideal gas from initial pressure  $P_1$  to final pressure  $P_1$  in four steps. The gas is allowed to expand against constant external pressure of  $P_1, P_2, P_3$  and  $P_4$  and finally  $P_1$ . Hence the system passes on to final state through four equilibrium states. The work done in the process is shown graphically. The area under the isotherm is the magnitude of reversible work. Clearly the magnitude of reversible work of expansion is greater than irreversible work. As the number of intermediate steps in irreversible expansion is increased, the magnitude of work increases, and as number of steps tend to infinity  $w_{irr}$  tends to  $w_{rev}$ . The graphical comparison of irreversible and reversible work is shown in fig.



- (D) **Free expansion of ideal gas :** When ideal gas is allowed to expand against zero external pressure, the process is called free expansion.  $W = 0$  for free expansion. During the free expansion, the ideal gas do not lose any energy, and hence temperature of ideal gas remains constant. Hence, free expansion of ideal gas is an example of isothermal, adiabatic irreversible process.

However if a real gas is allowed to expand in vacuum, the gas may be cooled or heated up depending upon temperature of the real gas. The temperature above which a gas gets heated up upon expansion is called **inversion temperature**.

#### Important points :

- If the reversible isothermal expansion is reversed by gradually increasing the pressure the system will return to initial state retracing it's path. This means path of reversible process can be exactly reversed if conditions are reversed.
- Work done by the system during reversible isothermal expansion is maximum possible work obtainable from system under similar condition.

#### Illustration

1. One mole of an ideal gas is expanded isothermally at 300 K from 10 atm to 1 atm. Calculate  $q$ ,  $w$ ,  $\Delta U$  &  $\Delta H$  under the following conditions.
  - (i) Expansion is carried out reversibly.
  - (ii) Expansion is carried out irreversibly

**Sol.** Isothermal process

(i) For ideal gas  $\Delta U = 0$        $\Delta H = 0$

$$q = -w$$

$$w_{\text{rev}} = -nRT \ln \frac{P_1}{P_r} = -1 \times R \times 300 \ln \frac{10}{1} = -690.9R$$

$$(ii) W_{\text{irrev}} = -P_{\text{ext}}(V_2 - V_1) = -P_{\text{ext}} \left( \frac{nRT}{P_2} - \frac{nRT}{P_1} \right) = -1 \times 1 \times R \times 300 \left[ \frac{1}{1} - \frac{1}{10} \right] = -270R$$

2. One mol an ideal gas is expanded from (10 atm, 10 lit). (2 atm, 50 lit) isothermally. First against 5 atm then against 2 atm. Calculate work done in each step and compare it with single step work done.

Sol.  $P_1 \quad V_1 \xrightarrow{\text{Isothermal}} P_2 \quad V_2$   
 10 atm 10 lit 2 atm 50 lit.

(i) Work done against 5 atm pressure  $\left( P_1 \quad V_1 \longrightarrow P_2 \quad V_2 \right)$   
 10 atm 10 lit 5 atm 20 lit

$$\text{Vol. of system at 5 atm} = \frac{10 \times 10}{5} = 20 \text{ lit.}$$

$$W_{\text{irrev}} = -P_{\text{ext}}(V_2 - V_1) = -5(20 - 10) = -50 \text{ atm lit.}$$

(ii) Work done against 2 atm

$$P_1 \quad V_1 \longrightarrow P_2 \quad V_2$$

5 atm 20 lit 2 atm 50 lit.

$$W_{\text{irr.}} = -P_{\text{ext}}(V_2 - V_1) = -2 \times (50 - 20) = -60 \text{ atm lit.}$$

$$W_{\text{total}} = -50 - 60 = -110 \text{ atm lit.}$$

Total work done in single step.

$$P_1 \quad V_1 \longrightarrow P_2 \quad V_2$$

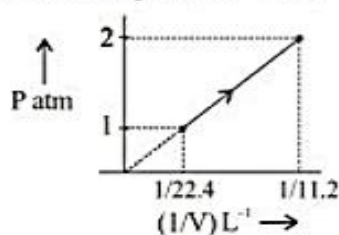
10 atm 10 lit 2 atm 50 lit.

$$w = -2(50 - 10) = -80 \text{ atm lit.}$$

Magnitude of work done in more than one step is more than single step work done.

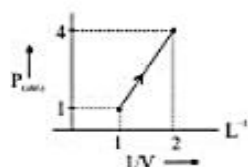
### Exercise

1. Calculate work done for an ideal gas ( $\ln 2 = 0.7$ )



Ans.  $w_{\text{rev}} = -nRT \ln \frac{V_2}{V_1} = -P_1 V_1 \ln \frac{V_2}{V_1} = -22.4 \ln \frac{1}{2} = 22.4 \times 0.7 = 15.68 \text{ L atm.}$

2. Calculate  $w = ? (\ln 2 = 0.7)$



Ans. P-V Relation from plot

$$P = \frac{3}{V} - 2 \Rightarrow w_{\text{rev}} = - \int P \, dv = - \int_1^2 \left( \frac{3}{V} - 2 \right) dv = 1.1 \text{ L atm.}$$

2. **Isobaric process** : In isobaric process, pressure remains constant during the process.

$$w = - \int_{V_1}^{V_2} P \, dV = - P_{\text{ext}} (V_2 - V_1) = - nR\Delta T \quad \& \quad \Delta H = q_p$$

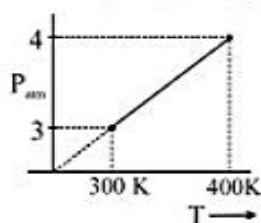
3. **Isochoric process** : In isochoric process, volume remains constant during the process.

$$\text{Since } dV = 0 \Rightarrow W = 0$$

$$\text{from 1st law} \quad \Delta U = q$$

### Illustration

1. For 1 mole of monoatomic gas. Calculate  $w, \Delta U, \Delta H, q$



Sol. Isochoric process

$$w = 0$$

$$q = dU = C_V (T_2 - T_1) = \frac{3}{2} \times (400 - 300) = 150 \text{ R}$$

$$\Delta H = C_P \Delta T = \frac{5}{2} \text{ R } (400 - 300) = 250 \text{ R}$$

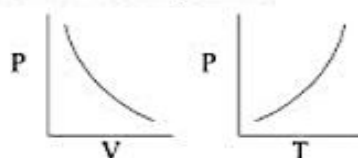
4. **Adiabatic process** : In adiabatic process, heat in interaction between system and surrounding is zero

$$q = 0, \quad W = nC_V (T_2 - T_1) = \frac{P_2 V_2 - P_1 V_1}{\gamma - 1}$$



Note :

1. For irreversible adiabatic process  $nC_v(T_2 - T_1) = -P_{\text{ext}} \left( \frac{nRT_2}{P_2} - \frac{nRT_1}{P_1} \right)$
2. Graphical representation of adiabatic process.



### Illustration

1. One mole of a non linear triatomic ideal gas is expanded adiabatically at 300 K from 16 atm to 1 atm. Calculate Work done under the following conditions.

(i) Expansion is carried out reversibly

(ii) Expansion is carried out irreversibly

Sol.  $q = 0$

$$w = \Delta U = C_v(T_2 - T_1)$$

$C_v$  for triatomic non linear gas =  $3R$

(i) For rev. process.

$$P_1^{1-\gamma} T_1^\gamma = P_2^{1-\gamma} T_2^\gamma \quad \gamma = \frac{4}{3}$$

$$T_2 = T_1 \left( \frac{P_1}{P_2} \right)^{\frac{1-\gamma}{\gamma}} = 300 (2^4)^{\frac{1}{4}} = 150 \text{ K}$$

$$\Delta U = w = 3R(150 - 300) = -450 R$$

(i)  $n = 1$

$$-P_{\text{ext}}(V_2 - V_1) = C_v(T_2 - T_1)$$

$$-P_{\text{ext}} \left( \frac{RT_2}{P_2} - \frac{RT_1}{P_1} \right) = 3R(T_2 - T_1)$$

$$-1 \left( \frac{RT_2}{1} - \frac{RT_1}{16} \right) = 3R(T_2 - T_1), \quad -\frac{R}{16}(16T_2 - T_1) = 3R(T_2 - T_1)$$

$$-16T_2 + T_1 = 48T_2 - 48T_1$$

$$49T_1 = 64T_2$$

$$T_2 = \frac{49}{64} \times 300 \Rightarrow T_2 = 229.69$$

$$w_{\text{irr}} = C_v(T_2 - T_1) + 3R(229.69 - 300) = -210.93 R$$

## Exercise

1. One mole of a non linear triatomic ideal gas is compressed adiabatically at 300 K from 1 atm to 16 atm. Calculate Work done under the following conditions.

- (i) Expansion is carried out reversibly  
(ii) Expansion is carried out irreversibly

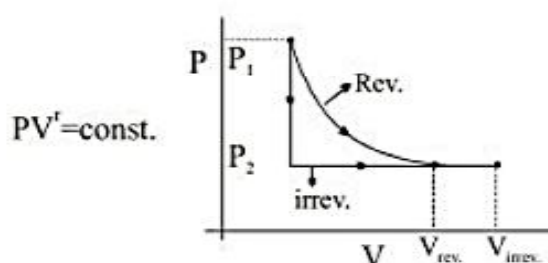
Ans. (i) 900 R (ii) 3375 R

## COMPARISON OF VARIOUS PROCESSES UNDER DEFINED CONDITIONS

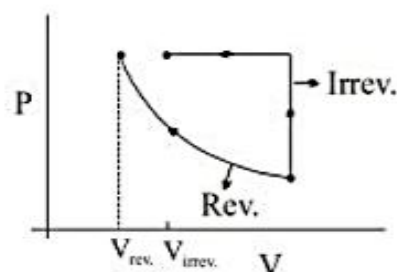
- (A) Graphical comparison between adiabatic reversible and irreversible process:

Case-I : For same final pressure

- (a) Expansion :

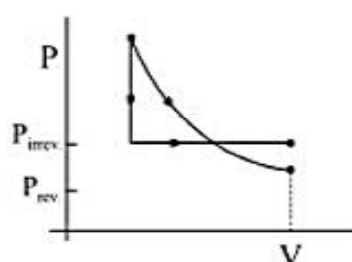


- (b) Compression :

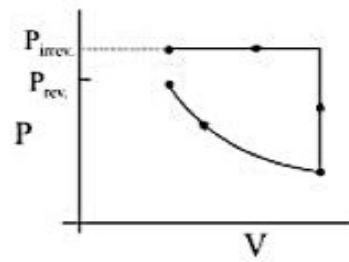


Case-II : For same final volume

- (a) Expansion



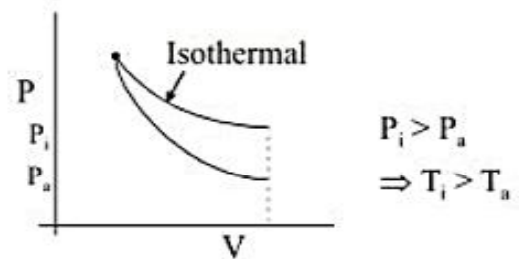
## (b) Compression



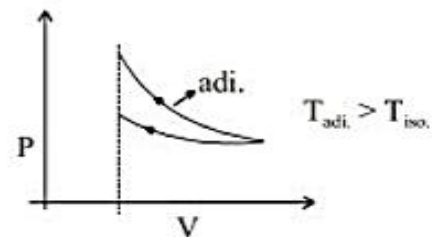
## (B) Comparison between isothermal &amp; adiabatic process:

Case-I : For same final volume

(a) Expansion :

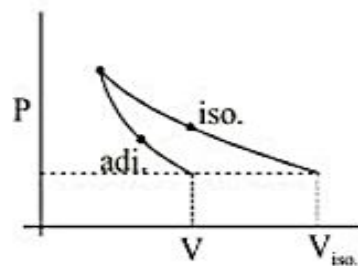


(b) Compression :

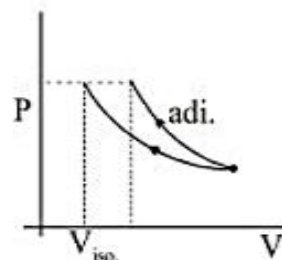


Case-II : For same final pressure

(a) Expansion

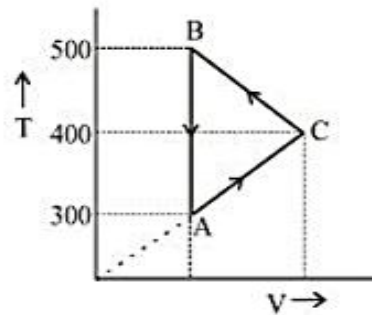


(b) Compression



### Illustration

1. Calculate work done in process BC for 1 mol of an ideal gas if total 600 cal heat is released by the gas in whole process



**Sol.** For cyclic process

$$dU = 0$$

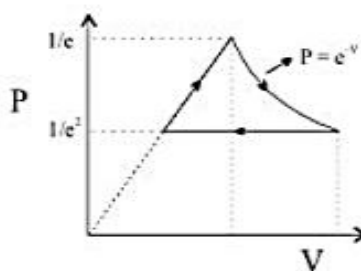
$$q = -w$$

$$q = -(w_{BA} + w_{AC} + w_{CB})$$

$$-600 = -(0 + (-) 2 \times (400 - 300) + w_{CB})$$

$$w_{CB} = 800 \text{ cal}$$

2.



**Sol.**  $w = ?$

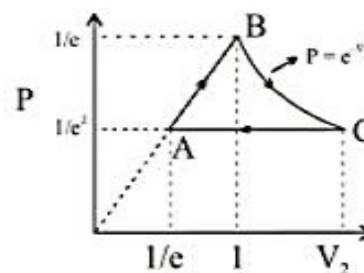
$$e^{-V}$$

$$P = KV$$

$$P = \frac{1}{e} V$$

$$\frac{1}{e^2} = KV_1$$

$$\frac{1}{e} = KV_2$$



$$\text{For AB } P = KV \Rightarrow P = \frac{1}{e} V \quad \frac{V_1}{V_2} = \frac{1}{e}$$

$$w_{AB} = - \int_{\frac{1}{e}}^1 \frac{1}{e} V dV = \frac{-1}{2e} \left[ 1 - \frac{1}{e^2} \right]$$



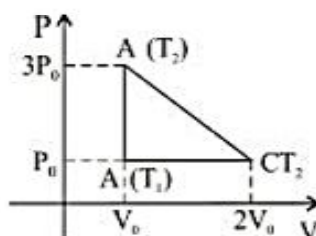
$$w_{BC} = -\int_1^2 e^{-v} dv = +[e^{-v}]_1^2 = +[e^{-2} - e^{-1}] = \frac{-1}{e} + \frac{1}{e^2}$$

$$w_{CA} = -\frac{1}{e^2} \left( \frac{1}{e} - 2 \right) = \frac{-1}{e^3} + \frac{2}{e^2}$$

$$w_{\text{Total}} = w_{AB} + w_{BC} + w_{CA} = \frac{-1}{2e} + \frac{1}{2e^3} + \frac{1}{e^2} - \frac{1}{e} - \frac{1}{e^3} + \frac{2}{e^2} = \frac{-1}{2e^3} + \frac{3}{e^2} - \frac{3}{2e} ]$$

### Exercise

1. One mole of an ideal monoatomic gas is taken in cyclic process ABCA as shown in the figure



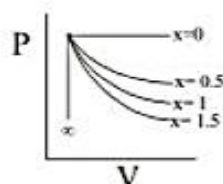
Calculate :

- The work done by the gas
- The heat rejected by the gas in the path CA
- The net heat absorbed by the gas in the path BC
- Maximum temperature obtained by the gas during the cycle.

Ans. (a)  $+3 P_0 V_0$       (b)  $-5/2 P_0 V_0$       (c)  $+P_0 V_0/2$       (d)  $+3 P_0 V_0/R$

**Polytropic process :** For polytropic process, value of exponential constant are different for various process.

$$PV^x = \text{constant}$$



- $x = 0$ , Isobaric process
- $x = 1$ , Isothermal process
- $x = \gamma$ , Adiabatic process
- $x = \infty$ , Isochoric process

## SECOND LAW OF THERMODYNAMICS

The essence of first law is that all physical and chemical processes take place in such a manner that the total energy of the universe remain constant.

However, it is observed that all processes have a natural direction ,i.e. a direction in which they take place spontaneously. First law fails to answer this. Another feature of the spontaneous processes is that they proceed only until an equilibrium is achieved. The direction of a spontaneous process and that it eventually reaches equilibrium, can be understood on the basis of entropy concept introduced through the second law of thermodynamics.

**The second law can be expressed in alternative forms as below :**

**(A) Clausius statement**

Clausius is credited with the first formulation of the second law, now known as the Clausius statement  
***"No process is possible whose sole result is the transfer of heat from a body of lower temperature to a body of higher temperature."***

Spontaneously, heat cannot flow from cold regions to hot regions without external work being performed on the system, which is evident from ordinary experience of refrigeration, for example. In a refrigerator, heat flows from cold to hot, but only when forced by an external agent, a compressor.

**(B) Kelvin statement**

The Kelvin statement expressed the second law in another form :

***"No process is possible in which the sole result is the absorption of heat from a reservoir and its complete conversion into work."***

This means it is impossible to extract energy by heat from a high-temperature energy source and then convert all of the energy into work. At least some of the energy must be passed on to heat a low-temperature energy sink. Thus, a heat engine with 100% efficiency is thermodynamically impossible.

This also means that it is impossible to build solar panels that generate electricity solely from the infrared band of the electromagnetic spectrum without consideration of the temperature on the other side of the panel (as is the case with conventional solar panels that operate in the visible spectrum).

Note that it is possible to convert heat completely into work, such as the isothermal expansion of ideal gas. However, such a process has an additional result. In the case of the isothermal expansion, the volume of the gas increases and never goes back without outside interference.

**Corollaries:****(A) Perpetual motion of the second kind**

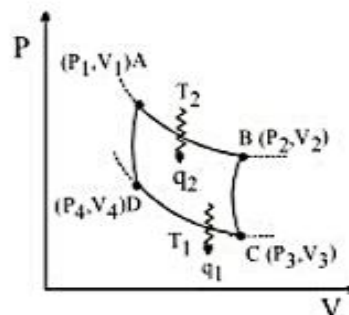
Prior to the establishment of the Second Law, many people who were interested in inventing a perpetual motion machine had tried to circumvent the restrictions of First Law of Thermodynamics by extracting the massive internal energy of the environment as the power of the machine. Such a machine is called a "perpetual motion machine of the second kind". The second law declared the impossibility of such machines.

**(B) Carnot theorem**

Carnot's theorem is a principle that limits the maximum efficiency for any possible engine. The efficiency solely depends on the temperature difference between the hot and cold thermal reservoirs. Carnot's theorem states:

- \* All irreversible heat engines between two heat reservoirs are less efficient than a Carnot engine operating between the same reservoirs.
- \* All reversible heat engines between two heat reservoirs are equally efficient with a Carnot engine operating between the same reservoirs.

**The thermodynamic cycle for carnot engine is given below :**

**Carnot cycle**

AB – Isothermal reversible expansion  $q_2 = -w_{AB} = nRT_2 \ln \frac{V_2}{V_1}$

BC – adiabatic reversible expansion  $w_{BC} = C_V (T_1 - T_2)$

CD – Isothermal reversible compression  $q_1 = -w_{CD} = nRT_1 \ln \left( \frac{V_4}{V_3} \right)$

DA – adiabatic reversible compression  $w_{DA} = C_V (T_2 - T_1)$

Carnot efficiency  $\eta = \frac{-w_{Total}}{q_2} = \frac{q_1 + q_2}{q_2} = \frac{T_2 - T_1}{T_2}$

$\frac{q_1}{T_1} + \frac{q_2}{T_2} = 0$  for rev. cycle

$\oint \frac{q_{rev}}{T} = \oint dS = 0$

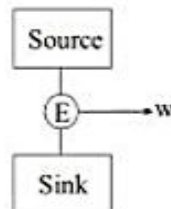


Entropy (denoted by  $S$ ) is a state function.

$$\Delta S = \int \frac{q_{\text{rev}}}{T}$$

### Statements of second law of thermodynamics

- (i) No cyclic engine is possible which take heat from one single source and in a cycle completely convert it into work without producing any change in surrounding.



### Illustration

1. Calculate maximum ' $\eta$ ' for an heat engine operating between  $27^\circ\text{C}$  to  $127^\circ\text{C}$ .

Sol.  $\eta = \frac{T_2 - T_1}{T_2} = \frac{400 - 300}{400} = 25\%$

## ENTROPY

Entropy is a thermodynamic property that can be used to determine the energy available for useful work in a thermodynamic process, such as in energy conversion devices. In thermodynamics, entropy is commonly associated with the amount of order, disorder, of a thermodynamic system.

$$dS = \frac{dq_{\text{rev}}}{T}$$

Thermodynamic entropy has the dimension of energy divided by temperature, and a unit of joules per Kelvin (J/K) in the International System of Units

To highlight the importance and developing below are various definitions of entropy:

- Entropy - a measure of the unavailability of a system's energy to do work; also a measure of disorder; the higher the entropy the greater the disorder.
- Entropy - a measure of disorder; the higher the entropy the greater the disorder.
- Entropy - in thermodynamics, a parameter representing the state of disorder of a system at the atomic, ionic, or molecular level; the greater the disorder the higher the entropy.

### Properties of entropy change ( $\Delta S$ ) :

1. The value of the entropy of a system of atoms and molecules in a thermodynamic system is a measure of the disorder in the arrangements of its particles.
2. In solids, which are typically ordered on the molecular scale, usually have smaller entropy than liquids, and liquids have smaller entropy than gases and colder gases have smaller entropy than hotter gases.



3. Moreover, according to the third law of thermodynamics, at absolute zero temperature, crystalline structures are approximated to have perfect "order" and zero entropy.
4. Entropy and disorder also have associations with equilibrium. Entropy, from this perspective, is defined as a thermodynamic property which serves as a measure of how close a system is to equilibrium
5. In a stretched out piece of rubber, the arrangement of the molecules of its structure has an "ordered" distribution and has zero entropy, while the "disordered" kinky distribution of the atoms and molecules in the rubber in the non-stretched state has positive entropy
6. In a gas, the order is perfect and the measure of entropy of the system has its lowest value when all the molecules are in one place, whereas when more points are occupied the gas is all the more disorderly and the measure of the entropy of the system has higher value
7. The mathematical basis with respect to the association entropy has with order and disorder is given by famous Boltzmann formula:

$$S = k \ln W$$

Which relates entropy  $S$  to the number of possible states  $W$  in which a system can be found

8. It is obvious that entropy is a measure of order or, most likely, disorder in the system. Second law of thermodynamics, as famously enunciated by Clausius in 1865, states that: "The entropy of the universe tends to a maximum"
9. Entropy is also a measure of the tendency of a process, such as a chemical reaction, to be entropically favored, or to proceed in a particular direction

### Physical significance of entropy

One can think entropy as a measure of the degree of randomness or disorder in a system. The greater the disorder, in a system, the higher is the entropy.

*Prediction of sign of  $\Delta S$  using the concept of Randomness.*

- (i) With change in temperature at constant 'V'

$$\text{As } T \uparrow \Rightarrow S \uparrow \Rightarrow \Delta S_{\text{sys}} > 0$$

- (ii) Change in volume at constant  $T$

$$\text{As } V \uparrow \Rightarrow S \uparrow \Rightarrow \Delta S_{\text{sys}} > 0$$

- (iii) For phase change

$$S_{\text{solid}} < S_{\text{liquid}} < S_{\text{gas}}$$

- (iv) In chemical reaction, entropy change ( $\Delta S$ )

- (a) Involving only solids and liquids entropy change will be small

eg. entropy of graphite > diamond (only when we know the structure or any other property).

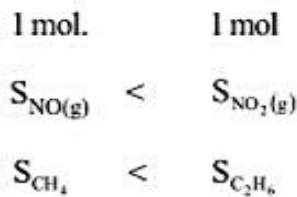
- (b) Involving gases

$$\text{If } (\Delta n)_g > 0 \Rightarrow (\Delta S) > 0$$

$$\text{If } (\Delta n)_g < 0 \Rightarrow (\Delta S) < 0$$

$$\text{If } (\Delta n)_g = 0 \Rightarrow (\Delta S) \neq 0$$

(v) As atomicity ↑ disorder ↑



(vi) For the molecules having same atomicity, entropy will be more for the substance having more molecular mass.

(vii) In an irreversible process entropy of universe increases but it remains constant in a reversible process.

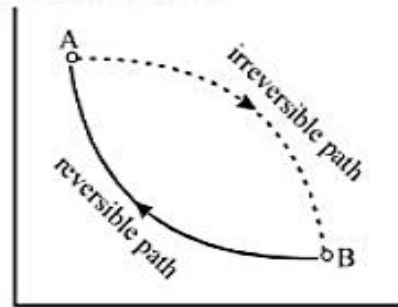
$$\Delta S_{\text{syt}} + \Delta S_{\text{surr}} = 0 \quad \text{for rev. process}$$

$$\Delta S_{\text{syt}} + \Delta S_{\text{surr}} > 0 \quad \text{for irrev. process}$$

$$\Delta S_{\text{syt}} + \Delta S_{\text{surr}} \geq 0 \quad (\text{In general})$$

### Entropy change in isolated system (isolated system = sys + surr)

Consider a system taken state A to state B by an irreversible path and returned to state A by a reversible path. Since one of the step is irreversible, according to classius inequality, sum of  $q/T$  over the cycle must be less than zero. Hence



$$\sum_{A \rightarrow B} \frac{q_{\text{irr}}}{T} + \sum_{B \rightarrow A} \frac{q_{\text{rev}}}{T} \leq 0 \Rightarrow \sum_{A \rightarrow B} \frac{q_{\text{irr}}}{T} \leq - \sum_{B \rightarrow A} \frac{q_{\text{rev}}}{T}$$

But  $-\sum_{B \rightarrow A} \frac{q_{\text{rev}}}{T} = \sum_{A \rightarrow B} \frac{q_{\text{rev}}}{T}$  since the process is reversible for infinitesimally small change

$$\left( \frac{dq_{\text{rev}}}{T} \right)_{A \rightarrow B} = dS_{\text{system} A \rightarrow B}$$

$$dS_{\text{system}} - \left( \frac{dq}{T} \right)_{A \rightarrow B} > 0$$

$$dS_{\text{system} A \rightarrow B} + dS_{\text{surr} A \rightarrow B} > 0$$

$$\Delta S_{\text{Total isolated sys}} > 0$$

Entropy calculation in process involving ideal gases.

From First law

$$dq = dU + PdV$$

$$\Rightarrow \frac{dq_{\text{rev}}}{T} = \frac{dU}{T} + \frac{PdV}{T}$$

But for ideal gas

$$\frac{dU}{T} = \frac{nC_V dT}{T} \quad \{\because dU = nC_V dT\}$$

$$\Rightarrow dS_{\text{sys}} = \frac{nC_V dT}{T} + \frac{nR}{V} dV$$

Integration gives

$$\Delta S = nC_V \ln \frac{T_2}{T_1} + nR \ln \left( \frac{V_2}{V_1} \right)$$

General Expression, for any process

$$\Delta S = nC_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1} = nC_P \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2}$$

**Entropy calculation for various process is given below.**

**(A) Isothermal process**

Reversible & irreversible isothermal expansion and contraction of an ideal gas

$$\Delta S_{\text{sys}} = nR \ln \frac{V_2}{V_1}$$

For surroundings

$$\Delta S_{\text{surr}} = -\Delta S_{\text{sys}} \text{ (for reversible)}$$

$$\Delta S_{\text{surr}} = \frac{q_{\text{surr}}}{T} \text{ (for irreversible)}$$

**(B) Isobaric process**

$$\Delta U = C_V \Delta T$$

$$\Delta H = C_P \Delta T = q_P$$

$$\Delta S_{\text{sys}} = nC_P \ln \left( \frac{T_2}{T_1} \right)$$

For surroundings

$$\Delta S_{\text{surr}} = -\Delta S_{\text{sys}} \text{ (for reversible)}$$

$$\Delta S_{\text{surr}} = \frac{q_{\text{surr}}}{T} \text{ (for irreversible)}$$

**(C) Isochoric process**

$$\Delta U = C_V \Delta T = q_V$$

$$\Delta H = C_P \Delta T$$

$$\Delta S_{\text{sys}} = nC_V \ln \left( \frac{T_2}{T_1} \right)$$

For surroundings

$$\Delta S_{\text{surr}} = -\Delta S_{\text{sys}} \text{ (for reversible)}$$

$$\Delta S_{\text{surr}} = \frac{q_{\text{surr}}}{T} \text{ (for irreversible)}$$

**(D) Adiabatic process**

$$\Delta U = C_V \Delta T$$

$$\Delta H = C_P \Delta T$$

$$\Delta S_{\text{sys}} = nC_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1} \text{ for irreversible process}$$

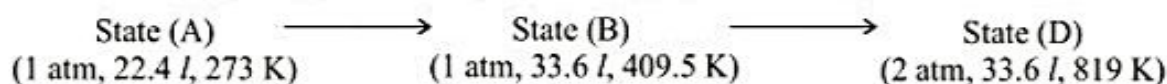
$\Delta S_{\text{sys}} = 0$  for reversible adiabatic compression and expansion.

For surroundings

$$\Delta S_{\text{surr}} = \frac{q_{\text{surr}}}{T} \text{ (for irreversible)}$$

**Illustration**

1. Calculate entropy change in each step for an ideal gas (monoatomic)



**Sol.**  $\Delta S_{A-B} = nC_P \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2} = nC_P \ln \frac{409.5}{273} = C_P \ln \frac{3}{2}$

$$\Delta S_{AC} = nC_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1} = C_V \ln \frac{546}{273} = C_V \ln 2$$

2. One mole of an ideal gas is expanded isothermally at 300 K from 10 atm to 1 atm. Find the values of  $\Delta S_{\text{sys}}$ ,  $\Delta S_{\text{surr}}$  &  $\Delta S_{\text{total}}$  under the following conditions.

(i) Expansion is carried out reversibly

(ii) Expansion is carried out irreversibly

(iii) Expansion is free.

**Sol.(i)**  $\Delta S_{\text{sys}} = nC_P \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2} = 0 + R \ln 10 = R \ln 10$

$$\Delta S_{\text{surr.}} = -\Delta S_{\text{sys}} = -R \ln 10$$

$$\Delta S_{\text{total}} = 0$$



$$(ii) \quad \Delta S_{\text{sys}} = R \ln 10$$

$$\Delta S_{\text{surr.}} = \frac{-q_{\text{irr}}}{T}$$

$$\Delta U = 0 = q + w$$

$$q_{\text{irr}} = p_{\text{ext}} (v_2 - v_1)$$

$$q_{\text{irr}} = p_{\text{ext}} \left[ \frac{RT}{p_2} - \frac{RT}{p_1} \right] = RT \left[ \frac{1}{1} - \frac{1}{10} \right] = RT \times \frac{9}{10} = \frac{9}{10} \times R \times 300 = 270R$$

$$\Delta S_{\text{surr}} = \frac{-q_{\text{irr}}}{T} = \frac{-9R}{10} \Rightarrow \Delta S_{\text{total}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = R \ln 10 - \frac{9R}{10}$$

$$(iii) \quad \text{Free expansion } \Delta T = 0$$

$$w = 0$$

$$q = 0$$

$$\Delta S_{\text{sys}} = R \ln 10$$

$$\Delta S_{\text{surr}} = \frac{-q_{\text{irr}}}{T} = 0$$

$$\Delta S_{\text{total}} = R \ln 10$$

### Exercise

1. One mole of an non linear triatomic ideal gas is expanded adiabatically at 300 K from 16 atm to 1 atm. Find the values of  $\Delta S_{\text{sys}}$ ,  $\Delta S_{\text{surr}}$  &  $\Delta S_{\text{total}}$  under the following conditions.

(i) Expansion is carried out reversibly

(ii) Expansion is carried out irreversibly

(iii) Expansion is free.

Ans. (i)  $\Delta S_{\text{sys}} = nC_v \ln \frac{T_2}{T_1} + nR \ln \frac{v_2}{v_1} = 0$ ,  $q = 0$ ,  $\Delta S_{\text{surr}} = -\Delta S_{\text{sys}} = \Delta S_{\text{total}} = 0$

(ii)  $\Delta S_{\text{sys}} = 1.702 R$ ,  $\Delta S_{\text{surr}} = 0$ ,  $\Delta S_{\text{total}} = \Delta S_{\text{sys}} = 1.702 R$

(iii)  $\Delta S_{\text{sys}} = nR \ln \frac{p_1}{p_2} = 2.77 R$ ,  $\Delta S_{\text{surr}} = \frac{-q_{\text{irr}}}{T} = 0$ ,  $\Delta S_{\text{total}} = \Delta S_{\text{sys}} = 2.77 R$

### (E) Entropy changes for the reactions

$$\Delta S_r = \sum v_p S (\text{products}) - \sum v_R S (\text{reactants})$$

Variation of  $\Delta S_r$  with temperature & pressure :

$$(\Delta S_r)_{T_2} - (\Delta S_r)_{T_1} = (\Delta C_p)_r \ln \frac{T_2}{T_1},$$

$$(\Delta S_r)_{p_2} - (\Delta S_r)_{p_1} = \Delta n_g R \ln \frac{p_1}{p_2}$$

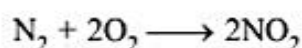
Similarly

$$(\Delta H_r)_{T_2} - (\Delta H_r)_{T_1} = (\Delta C_p)_r (T_2 - T_1) \quad \{\text{Krichoff's equation}\}$$

$$(\Delta U_r)_{T_2} - (\Delta U_r)_{T_1} = (\Delta C_p)_r (T_2 - T_1)$$

### Illustration

1. For the reaction



Given: at 1 atm, 300 K

$$S_{\text{N}_2} = 180 \text{ J/mol/K}$$

$$C_p(\text{N}_2) = 30 \text{ J/mol/K}$$

$$S_{\text{O}_2} = 220 \text{ J/mol/K}$$

$$C_p(\text{O}_2) = 30 \text{ J/mol/K}$$

$$S_{\text{NO}_2} = 240 \text{ J/mol/K}$$

$$C_p(\text{NO}_2) = 40 \text{ J/mol/K}$$

Calculate (i)  $\Delta S_{300 \text{ K}, 1 \text{ atm}}$

(ii)  $\Delta S_{400 \text{ K}, 1 \text{ atm}}$

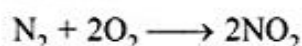
**Sol.(i)**  $(\Delta S_r)_{300} = 2S_{\text{NO}_2} - 2S_{\text{O}_2} - S_{\text{N}_2} = 2 \times 240 - 2 \times 220 - 180 = -140 \text{ J mol}^{-1} \text{ K}^{-1}$

$$(\Delta C_p)_r = 2C_p(\text{NO}_2) - 2C_p(\text{O}_2) - C_p(\text{N}_2) = 2 \times 40 - 2 \times 30 - 30 = -10 \text{ J mol}^{-1} \text{ K}^{-1}$$

(ii)  $(\Delta S_r)_{400} = (\Delta S_r)_{300} + (\Delta C_p)_r \ln \frac{T_2}{T_1} = -140 - 10 \ln \frac{4}{3} = -142.88 \text{ J mol}^{-1} \text{ K}^{-1}$

### Exercise

1. For the reaction



Given: at 1 atm, 300 K

$$S_{\text{N}_2} = 180 \text{ J/mol/K}$$

$$C_p(\text{N}_2) = 30 \text{ J/mol/K}$$

$$S_{\text{O}_2} = 220 \text{ J/mol/K}$$

$$C_p(\text{O}_2) = 30 \text{ J/mol/K}$$

$$S_{\text{NO}_2} = 240 \text{ J/mol/K}$$

$$C_p(\text{NO}_2) = 40 \text{ J/mol/K}$$

Calculate (i)  $\Delta S_{300 \text{ K}, 5 \text{ atm}}$

(ii)  $\Delta S_{400 \text{ K}, 5 \text{ atm}}$

**Ans.** (i)  $(\Delta S_r)_{300 \text{ K}, 5 \text{ atm}} = -126.62 \text{ J mol}^{-1} \text{ K}^{-1}$ .

(ii)  $(\Delta S_r)_{400 \text{ K}, 5 \text{ atm}} = -129.5 \text{ J K}^{-1} \text{ mol}^{-1}$ .

(F) **Entropy change during phase change :** During phase change and entropy change is measured as

$$\Delta S = \frac{\Delta H}{T}$$

### Illustration

1. Calculate entropy change



$$\Delta H_{\text{vap}} = 40 \text{ kJ/mol} \quad C_p(l) = 75 \text{ J/mol/K} \quad C_p(g) = 35 \text{ J/mol/K}$$

Sol.  $\text{H}_2\text{O} (l, 2 \text{ atm}, 100^\circ\text{C}) \longrightarrow \text{H}_2\text{O} (g, 1 \text{ atm}, 100^\circ\text{C}) \longrightarrow \text{H}_2\text{O} (g, 2 \text{ atm}, 100^\circ\text{C})$   
 (A) (B) (C)

$$\Delta S_{A \rightarrow B} = \frac{\Delta H_{\text{vap}}}{T} = \frac{40.000}{373}$$

$$\Delta S_{B \rightarrow C} = n R \ln \frac{P_2}{P_1} = 1 \times R \ln \frac{1}{2}$$

### Exercise

1. Calculate entropy change



$$\Delta H_{\text{vap}} = 40 \text{ kJ/mol} \quad C_p(l) = 75 \text{ J/mol/K} \quad C_p(g) = 35 \text{ J/mol/K}$$

Ans.  $\Delta S_{A \rightarrow B} = \frac{\Delta H_{\text{vap}}}{T} = \frac{40 \times 1000}{373}$ ,  $\Delta S_{B \rightarrow C} = n C_p(g) \ln \frac{T_2}{T_1} = 1 \times 35 \ln \frac{383}{373}$

## THIRD LAW OF THERMODYNAMICS

“At absolute zero, the entropy of a perfectly crystalline substance is taken as zero”, which means that at absolute zero every crystalline solid is in a state of perfect order and its entropy should be zero.

By virtue of the third law, the absolute value of entropy (unlike absolute value of enthalpy) for any pure substance can be calculated at room temperature.

$$S_T - S_{0K} = \int_0^T \frac{q_{\text{rev}}}{T}$$

since  $S_{0K} = 0$

$$S_T = \int_0^T \frac{q_{rev}}{T}$$

Absolute entropies of various substances have been tabulated and these value are used to calculate entropy changes for the reactions.

## GIBBS FREE ENERGY (G) AND SPONTANEITY

Gibbs free energy is a thermodynamics potential that measures the "useful" work obtainable from a thermodynamic system at a constant temperature and pressure. Alternatively, Gibbs energy is the capacity of a system to do non-mechanical work and  $\Delta G$  measures the non-mechanical work done on it.

The term "free" was attached to Gibbs free energy for systems at constant pressure and temperature to mean "available in the form of useful work. However, an increasing number of books do not include the attachment "free", referring to G as simply "Gibbs energy". In 1988 IUPAC meeting the term 'free' was dropped.

IUPAC recommended name: Gibbs energy or Gibbs function

The Gibbs free energy is mathematically defined as:

$$G(p,T) = U + pV - TS$$

which is the same as:

$$G(p,T) = H - TS$$

where:

U is the internal energy (SI unit: joule)

p is pressure (SI unit: pascal)

V is volume (SI unit: m<sup>3</sup>)

T is the temperature (SI unit: kelvin)

S is the entropy (SI unit: joule per kelvin)

H is the enthalpy (SI unit: joule)

### Properties of Gibbs free energy

1. The Gibbs free energy is the maximum amount of non-expansion work that can be extracted from a closed system ; this maximum can be attained only in a completely reversible process.
2. When a system changes from a well-defined initial state to a well-defined final state, the Gibbs free energy  $\Delta G$  equals the work exchanged by the system with its surroundings, minus the work of the pressure forces, during a reversible transformation of the system from the same initial state to the same final state.
3. Gibbs energy ( $\Delta G$ ) is also the chemical potential that is minimized when a system reaches equilibrium at constant pressure and temperature. Its derivative with respect to the reaction coordinate of the system becomes zero at the equilibrium point.



4. As such, it is a convenient criterion of spontaneity for processes with constant pressure and temperature.
5. The Gibbs free energy the greatest amount of mechanical work which can be obtained from a given quantity of a certain substance in a given initial state, without increasing its total volume or allowing heat to pass to or from external bodies, except such as at the close of the processes are left in their initial condition.
6. Every system seeks to achieve a minimum of free energy.
7. The energy released equals the maximum amount of work that can be performed as a result of the chemical reaction. In contrast, if conditions indicated a positive  $\Delta G$ , then energy in the form of work would have to be added to the reacting system to make the reaction proceed.
8. Thus the direction of reaction will only be allowed if the total entropy change of the universe is equal to zero (an equilibrium process) or positive and correspondingly gibbs free energy criteria is:
  - A.  $\Delta G > 0$  the process is non-spontaneous
  - B.  $\Delta G = 0$  system is at equilibrium
  - C.  $\Delta G < 0$  the process is spontaneous

A new thermodynamic state function  $G$ , the Gibbs free energy is defined as :

$$G = H - TS$$

at constant temperature and pressure

$$\Delta G = \Delta H - T \Delta S$$

- If
- |                        |   |
|------------------------|---|
| $(\Delta G)_{T,P} < 0$ | process is irreversible (spontaneous)   |
| $(\Delta G)_{T,P} = 0$ | process is reversible                   |
| $(\Delta G)_{T,P} > 0$ | process is impossible (non spontaneous) |

The use of Gibbs free energy has the advantage that it refers to the system only (and not surroundings).

To summaries, the spontaneity of a chemical reaction is decided by two factors taken together:

- (i) the enthalpy factor                      and                      (ii) the entropy factor.

The equation  $\Delta G = \Delta H - T \Delta S$  takes both the factors into consideration.

$(\Delta H_r)_{T,P}$	$(\Delta S_r)_{T,P}$	$(\Delta G_r)_{T,P}$	Remarks
- ve	+ ve	Always - ve	Reaction is spontaneous
+ ve	- ve	Always + ve	Reaction non spontaneous
+ ve	+ ve	At low temperature, $\Delta G = + ve$	Non spontaneous
		At high temperature, $\Delta G = - ve$	Spontaneous
- ve	- ve	At low temperature, - ve	Spontaneous
		At high temperature, +ve	Non spontaneous

### Variation of Gibb's function (G) with temperature and pressure :

$$G = H - TS$$

$$= U + PV - TS$$

$$dG = dU + PdV - TdS + VdP - SdT$$

$$dG = VdP - SdT$$

- (A) At constant temperature,  $dT = 0$   
for every substance

$$dG = VdP \quad \text{or} \quad \left( \frac{\partial G}{\partial P} \right)_T = V$$

- (i) For an ideal gas, at constant temperature

$$dT = 0 \quad \text{and} \quad V = \frac{nRT}{P}$$

So

$$dG = \frac{nRT}{P} dP = nRT \ln \frac{P_2}{P_1}$$

- (ii) For solids / liquids, at constant temperature

$dT = 0$  and  $V$  is almost constant change in pressure

So

$$dG = vdp \quad [v = \text{constant}]$$

$$\Delta G = v (P_2 - P_1)$$

- (B) At constant pressure,  $dP = 0$

For any substance

$$dG = -SdT$$

$$\left( \frac{\partial G}{\partial T} \right)_P = -S$$

If in a question, given that  $S = f(T)$ , by integrating  $\Delta G$  can be calculate.

### Relationship between $\Delta G$ & $W_{\text{non-PV}}$

Decrease in Gibb's function at constant temperature and pressure in a process given an estimate or measure of maximum non-PV work which can be obtained from system in reversible, manner.

The example of non-PV work is electric work done by chemical battery.

Expansion of soap bubble at for a closed system capable of doing non-PV work apart from PV work first law can be written as

$$dU = q + W_{\text{PV}} + W_{\text{non-PV}}$$

for reversible process at constant T & P

$$dU + pdV - TdS = W_{\text{non-PV}}$$

$$dH - TdS = W_{\text{non-PV}}$$

$$(dG_{\text{system}})_{T,P} = W_{\text{non-PV}}$$

$$-(dG_{\text{system}})_{T,P} = (W_{\text{non-PV}})_{\text{system}}$$

Non-PV work done by the system = decrease in gibbs free energy

Non-pV work done due to chemical energy transformation of due to composition change and decrease in Gibb's function in a isothermal and isobaric process provide a measure of chemical energy stored in bonds and intermolecular interaction energy of molecules.

### Some facts to be remembered :

(a) Standard condition

(i) For gases / solid / liquid : P = 1 bar

(ii) For ion / substance in solution : concentration = 1 M

$$(b) \quad \Delta G_r = (\Delta G_f)_{\text{product}} - (\Delta G_f)_{\text{reactant}}$$

$$\Delta H_r = (\Delta H_f)_{\text{product}} - (\Delta H_f)_{\text{reactant}}$$

$$\Delta S_r = (\Delta S_f)_{\text{product}} - (\Delta S_f)_{\text{reactant}}$$

### THERMODYNAMIC RELATIONSHIP BETWEEN $\Delta G$ AND EQUILIBRIUM CONSTANT

$$\Delta G = RT \ln \frac{p_2}{p_1}$$

$$G_2 = G_1 + RT \ln \frac{p_2}{p_1}$$

$$G_2 = G^\circ + RT \ln \frac{p_2}{1 \text{ bar}}$$

Consider a reaction  $A + B \longrightarrow C$

$$G_A = G_A^\circ + RT \ln \frac{p_A}{1 \text{ bar}}$$

$$G_B = G_B^\circ + RT \ln \frac{p_B}{1 \text{ bar}}$$

$$G_C = G_C^\circ + RT \ln \frac{p_C}{1 \text{ bar}}$$

$$\Delta G_r = G_r^\circ + RT \ln \frac{P_C}{\left(\frac{P_A}{\text{lbar}}\right)\left(\frac{P_B}{\text{lbar}}\right)}$$

$$\Delta G_r = \Delta G_r^\circ + RT \ln Q \quad [Q = \text{Reaction quotient}]$$

$$\Delta G_r^\circ = -RT \ln K_{\text{eq}} \quad (\text{At eq}^m, (\Delta G_r)_{T,P} = 0)$$

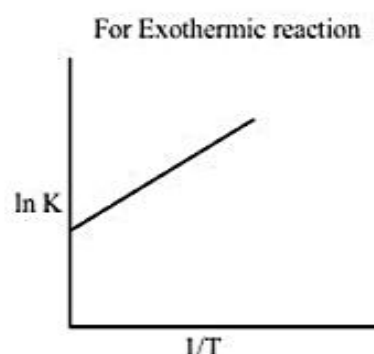
$$\Delta G_r^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\ln K_{\text{eq}} = \frac{-\Delta_r H^\circ}{RT} + \frac{\Delta_r S^\circ}{R}$$

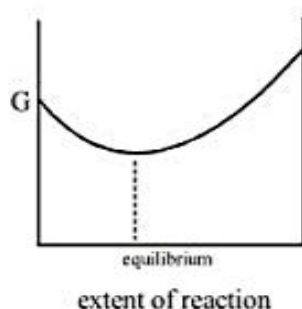
$$\ln K_1 = \frac{\Delta_r S^\circ}{R} - \frac{\Delta_r H^\circ}{RT_1}$$

$$\ln K_2 = \frac{\Delta_r S^\circ}{R} - \frac{\Delta_r H^\circ}{KT_2}$$

$$\ln \left( \frac{K_2}{K_1} \right) = \frac{\Delta H^\circ}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$



- \* **For a chemical reaction :** During a chemical reaction, reaction proceeds in that direction in which  $\Delta G < 0$  or value of  $G$  decreases and attains lowest value at equilibrium condition as show in the figure. More ever as equilibrium condition is changed in either direction, reaction always proceeds towards equilibrium condition



**Clausius Inequality :** Clausius inequality is another way for measuring the irrversibility and spontaneity of a process.

In mathematical as term, it can be expressed as-

$$Tds \geq q$$

$$Tds \geq dU - w$$

at constant temperature & pressure

$$d(U - TS + PV) \leq 0$$

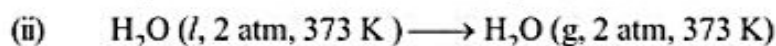
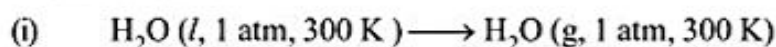
$$(H - TS) \leq 0$$

$$dG \leq 0$$



**Illustration**

1. Calculate  $\Delta G$  for



Given :  $\Delta H_{373} = 40 \text{ kJ}$

$C_p(\text{H}_2\text{O}, l) = 75 \text{ J / mol / K}$

$C_p(\text{H}_2\text{O}, g) = 35 \text{ J / mol / K}$

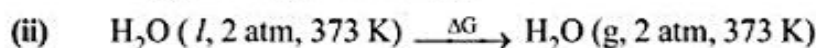
Sol.(i)  $\Delta H_{300} - \Delta H_{373} = (-40) (-73)$

$\Delta H_{300} = 42920$

$\Delta S_{373} = \frac{40 \times 10^3}{373}$

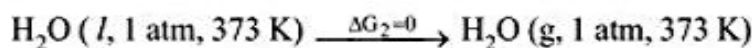
$\Delta S_{300} = \Delta S_{373} + 40 \ln \frac{373}{300}$

$\Delta G_{300} = \Delta H_{300} - 300 \Delta S_{300}$



$\downarrow \Delta G_1 = [V(1-2)]$

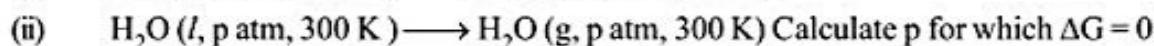
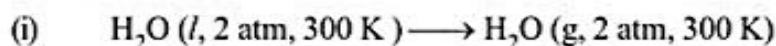
$\uparrow \Delta G_3 = nRT \ln \frac{2}{1}$



$\Delta G = V(1-2) + \Delta G_2 + nRT \ln \frac{2}{1}$

**Exercise**

1. Calculate  $\Delta G$  for



Given :  $\Delta H_{373} = 40 \text{ kJ}$

$C_p(\text{H}_2\text{O}, l) = 75 \text{ J / mol / K}$

$C_p(\text{H}_2\text{O}, g) = 35 \text{ J / mol / K}$

Ans. (i)  $\Delta G = V(P_2 - P_1) + [\Delta H_{300} - 300 \Delta S_{300}] + nRT \ln \frac{P_2}{P_1}$

(ii)  $P = 26.28 \text{ atm}$

## SOLVED EXAMPLE

**Q.1** Value of  $\gamma$  for  $\text{CH}_4$  molecule is (Consider vibrational degree of freedom to be active)

- (A)  $\frac{4}{3}$                       (B)  $\frac{13}{12}$                       (C)  $\frac{15}{14}$                       (D)  $\frac{17}{15}$

**Ans. (B)**

**Sol.**  $C_V = 3R + 9R \Rightarrow 12R$

$$C_P = 13R$$

$$\gamma = \frac{C_P}{C_V} = \frac{13}{12}$$

**Q.2** ' $\gamma$ ' for  $\text{NH}_3$  including contribution from vibrational degree's of freedom is

- (A)  $\frac{4}{3}$                       (B)  $\frac{10}{9}$                       (C)  $\frac{7}{6}$                       (D)  $\frac{13}{12}$

**Ans. (B)**

**Sol.**  $C_V = \frac{n_{tr}}{2}R + \frac{n_{rot}}{2}R + n_{vib}R = \frac{3}{2}R + \frac{3}{2}R + 6R = 9R$

$$C_P = 9R + R = 10R$$

$$\gamma = \frac{C_P}{C_V} = \frac{10}{9}$$

**Q.3** 1 mole of an ideal gas is expanded isothermally and reversibly from 1 litre to 100 litre. Which of the following is false for the process?

- (A)  $\Delta T = 0$                       (B)  $\Delta E = 0$                       (C)  $\Delta H = 0$                       (D) heat supplied ( $q$ ) = 0

**Ans. (D)**

**Hint:** For isothermal process involving ideal gas  $\Delta T = \Delta E = \Delta H = 0$

**Q.4** Pressure over 1 litre of a liquid is gradually increases from 1 bar to 1001 bar under adiabatic condition. If the final volume of the liquid is 990 ml, calculate  $\Delta E$  and  $\Delta H$  of the process assuming linear variation of volume with pressure.

**Sol.** Assuming linear variation of volume with pressure

$$W = \text{area under the show line} = (10 \times 10^{-6} \text{m}^3) \times (10^5 \text{N/m}^2) + \frac{1}{2} (1000 \times 10^5 \text{N/m}^2) \times (10 \times 10^{-6} \text{m}^3)$$

$$= 1 \text{ J} + 500 \text{ J} = 501 \text{ Joule}$$

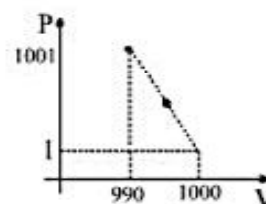
$$\Delta E = 501 \text{ Joule}$$

$$\Delta H = \Delta E + P_2 V_2 - P_1 V_1$$

$$= 501 \text{ J} + (1001 \times 10^5 \text{ N/m}^2) \times (990 \times 10^{-6} \text{m}^3) - (1 \times 10^5 \text{ N/m}^2) \times (1000 \times 10^{-6} \text{m}^3)$$

$$= 501 \text{ J} + (99 \times 1001 \text{ J}) - (100 \text{ J})$$

$$= 99.5 \text{ kJ} \quad \text{Ans.}$$



**Q.5** One mole of a real gas is subjected to a process from (2 bar, 30 lit., 300 K) to (2 bar, 40 lit., 500 K)

Given :  $C_v = 25 \text{ J/mol/K}$

$C_p = 40 \text{ J/mol/K}$

Calculate  $\Delta U$ .

(A) 5000 J

(B) 6000 J

(C) 8000 J

(D) 10000 J

**Ans. (B)**

**Sol.**  $\Delta U = q + w$   
 $= (40 \times 200) + (-2 \times 10 \times 100)$   
 $= 6000 \text{ J Ans.}$

**Q.6** One mole of ideal gas undergoes following cyclic process:

(I) Isochoric heating from  $(P_1, V_1, T_1)$  to double temperature.

(II) Isobaric expansion from to double volume.

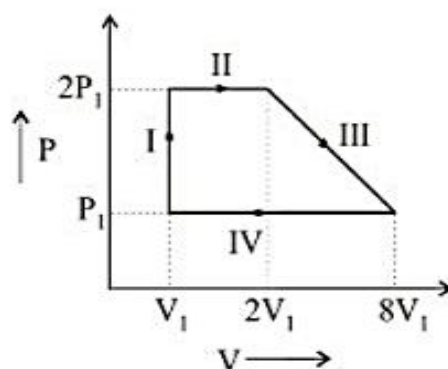
(III) Linear expansion (on PV curve) to  $(P_1, 8V_1)$ .

(IV) Isobaric compression to initial state.

Calculate the magnitude of work done in calories if initial temperature of the gas is 300 K?

Given :  $R = 2 \frac{\text{Cal}}{\text{mol-K}}$

**Sol.** Magnitude of work =  $A = P_1 V_1 + \frac{1}{2} \times P_1 \times 6 V_1$   
 $= 4 P_1 V_1 = 4 nRT_1$   
 $= 4 \times 1 \times 2 \times 300$   
 $= 2400 \text{ cal}$

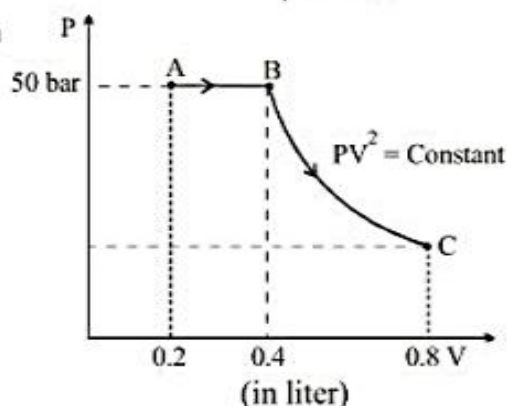


**Q.7** Determine the total work done by a gas (in Joule) if system follows an expansion process as shown in figure.

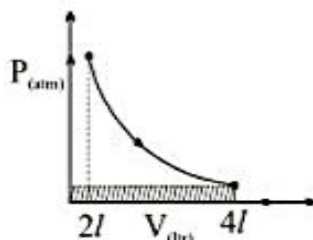
[Given : 1 Bar liter = 100 J]

**Sol.**  $P_B V_B^2 = P_C V_C^2$   
 or  $50 \times (0.4)^2 = P_C \times (0.8)^2$   
 or  $P_C = \frac{50 \times 0.4 \times 0.4}{0.8 \times 0.8} = 12.5$

$w = w_{AB} + w_{BC}$   
 $= -50 (0.4 - 0.2) + \frac{P_C V_C - P_B V_B}{2 - 1}$   
 $= -50 \times 0.2 + \frac{12.5 \times 0.8 - 50 \times 0.4}{1}$   
 $= -10 + (-10) = -20 \text{ bar liter} = -2000 \text{ J}$   
 $w_{by} = 2000 \text{ J}$



- Q.9** A student is calculating the work during a reversible isothermal process, shown by 2 moles of an ideal gas. He by mistake calculated the area as shown in the PV graph (Shaded area) equal to 49.26 litre atm. Calculate the correct value of work (in litre atm) during the process.  
(Given :  $R = 0.0821$  litre atm/mol/K)



- (A) 49.26                      (B) - 34.14                      (C) - 78.63                      (D) - 98.52

**Sol.** For isothermal process

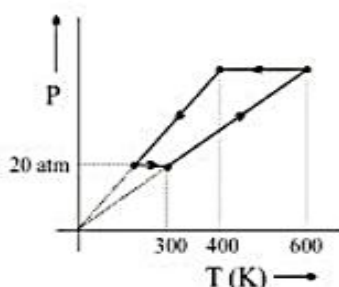
$$W = -nRT \ln \frac{V_2}{V_1}$$

$$= -49.26 \times \ln 2$$

$$= -34.14$$

$$[\text{Shaded area} = PV = nRT]$$

- Q.10** Calculate the magnitude of work done (in atm lit.) for the given cyclic process involving 1 mol of an ideal gas. [Given :  $R = 0.08$  atm lit./mol/K]



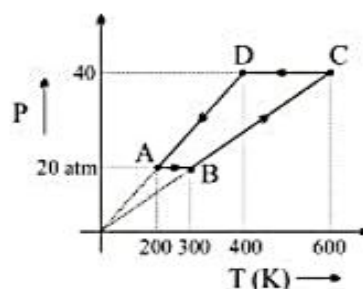
**Sol.**  $W_{AB} = W_{CD} = 0$

$$W_{BC} = -nR\Delta T = -1 \times R \times 300 = 300 R$$

$$W_{DA} = -nR\Delta T = -1 \times R \times -200 = 200 R$$

$$W_{\text{total}} = -100 R$$

$$\Rightarrow |W| = 8 \text{ lit atm}$$



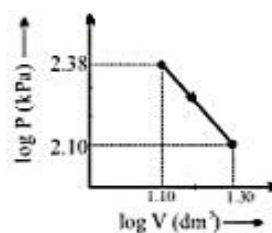
- Q.11** log P vs log V curve is plotted for an ideal gas, which is true for the gas?

- (A) Monoatomic & undergoing adiabatic change  
(B) Monoatomic & undergoing an isothermal change  
(C) Diatomic & undergoing an adiabatic change  
(D) Triatomic & undergoing an isothermal change

**Ans.** (C)

**Sol.** Equation of process

$$\frac{\log P - 2.38}{\log V - 1.10} = \frac{2.10 - 2.38}{1.30 - 1.10} = \frac{-0.28}{0.20} = \frac{-7}{5}$$





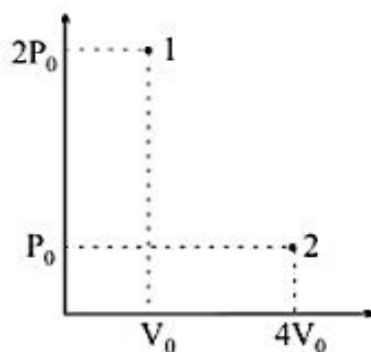
$$\begin{aligned}
 &\Rightarrow (\log P - 2.38) \times 5 = -7 (\log V - 1.1) \\
 &\Rightarrow 5 \log P + 7 \log V = 19.60 \\
 &\Rightarrow \log P^5 + \log V^7 = 19.60 \\
 &P^5 V^7 = \text{antilog}(19.60) = \text{constant} \\
 &\text{or } PV^{1.4} = \text{constant} \\
 &\therefore \gamma = 1.4 - \text{diatomic \& adiabatic}
 \end{aligned}$$

- Q.12** A certain mass of a gas is expanded from (1L, 10 atm) to (4L, 5 atm) against a constant external pressure of 1 atm. If initial temperature of gas is 300 K and the heat capacity of process is 50 J/°C. Calculate  $\Delta H$  (in kJ) of the process. (Given 1L atm = 100 J).  
(Fill your answer by multiplying it with 100)

**Sol.**  $\Delta U = Q + W$

$$\begin{aligned}
 &\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \\
 &= 50 \times (600 - 300) - 1(4 - 1) \times 100 \quad \text{or} \quad \frac{10 \times 1}{300} = \frac{5 \times 4}{T_2} \\
 &= 15000 - 300 \text{ J} \quad \text{or} \quad T_2 = 5 \times 4 \times 30 = 600 \text{ K} \\
 &= 14700 \text{ J} \\
 &= 14.7 \text{ J} \\
 &\Delta H = \Delta U + (P_2 V_2 - P_1 V_1) \\
 &= 14.7 + \frac{(20 - 10) \times 100}{1000} \\
 &= 14.7 + 1 = 15.7 \text{ kJ} = 1570
 \end{aligned}$$

- Q.13** A liquid confined inside an adiabatic container is suddenly taken from state 1 to state 2 by a single stage process as shown, then  $\Delta H$  is



(A)  $\Delta H = \frac{2\gamma P_0 V_0}{\gamma - 1}$     (B)  $\Delta H = -P_0 V_0$     (C)  $\Delta H = -3P_0 V_0$     (D)  $\Delta H = \frac{3\gamma P_0 V_0}{\gamma - 1}$

**Ans. (B)**

**Sol.**  $Q = 0$   
 $\Delta U = Q + w = w$   
 $w = -P_0(4V_0 - V_0) = -3P_0 V_0$   
 $\Delta H = \Delta U + (P_2 V_2 - P_1 V_1)$   
 $= -3P_0 V_0 + (4P_0 V_0 - 2P_0 V_0)$   
 $= -3P_0 V_0 + 2P_0 V_0$   
 $= -P_0 V_0$

**Q.14** One mole of Argon is heated using  $PV^{5/2} = \text{constant}$ . By what amount heat is absorbed during the process, when temperature changes by  $\Delta T = 26 \text{ K}$ .

- (A) 100 J (B) 200 J (C) 180 J (D) 208 J

**Ans.** (C)

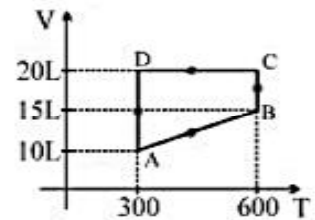
**Sol.**  $n = 1$   $C_v = \frac{3}{2} R$ .  $PV^{5/2} = \text{constant}$ ,  $n' = 5/2$

$$q = n C \Delta T$$

$$= n \left[ C_v + \frac{R}{1-n'} \right] \Delta T = 1 \left[ \frac{3}{2} R + \frac{R}{1-\frac{5}{2}} \right] 26 = \left[ \frac{3}{2} R - \frac{2}{3} R \right] 26 = \frac{5}{6} R \times 26 = \frac{5 \times 8.314 \times 26}{6} = 180 \text{ J}$$

**Q.15** One mole monoatomic ideal gas was taken through process ABCD as shown in figure. Calculate

- (i)  $w_{AB}$ ,  $w_{BC}$ ,  $w_{CD}$ ,  $w_{DA}$   
 (ii)  $q_{AB}$ ,  $q_{BC}$ ,  $q_{CD}$ ,  $q_{DA}$   
 (iii)  $\Delta H_{AB}$ ,  $\Delta H_{BC}$ ,  $\Delta H_{CD}$ ,  $\Delta H_{DA}$   
 [Use :  $\ln(3/2) = 0.40$  ;  $\ln(4/3) = 0.29$ ]



**Sol.(i)**  $w_{AB}$  : Along 'AB' pressure is variable

$$\text{from graph : } \frac{V-10}{T-300} = \frac{15-10}{600-300} \Rightarrow 60V - 600 = T - 300 \Rightarrow 60V - 300 = T$$

sub value of T in ideal gas equation

$$PV = R(60V - 300) \Rightarrow P = 60R - \frac{300R}{V}$$

$$w_{AB} = - \int_{10}^{15} P dV = - \int_{10}^{15} \left[ 60R - \frac{300R}{V} \right] dV = -60R(V_2 - V_1) + 300R \ln \left( \frac{V_2}{V_1} \right)$$

$$= -300R + 300R(0.4) \quad (\text{take } \ln(3/2) = 0.40 \text{ data})$$

$$w_{AB} = -180R = -1496.52 \text{ J Ans.}$$

$$w_{BC} = -RT \ln \frac{V_3}{V_2} = -RT \ln(4/3) \quad (\text{take } \ln(4/3) = 0.29 \text{ data})$$

$$= -8.314 \times 600 \times 0.29 = -1446.63 \text{ Joule Ans.}$$

$$w_{CD} = 0 \text{ Ans.}$$

$$w_{DA} = -nRT \ln \frac{V_1}{V_3} = -1 \times 8.314 \times 300 \ln \left( \frac{10}{20} \right) = +1728.84 \text{ Joule Ans.}$$

**(ii)**  $q_{AB} = \Delta E_{AB} - w = \frac{3}{2} R \times 300 + 1496.52 = 450 R + 180 R = 630 R = 5237.82 \text{ Joule Ans.}$

$$q_{BC} = -w_{BC} = +1446.63 \text{ Joule Ans.}$$

$$q_{CD} = \Delta U = n C_v \Delta T = 1 \times \frac{3}{2} R \times (300-600) = -3741.3 \text{ Joule Ans.}$$

$$q_{DA} = -w_{DA} = 1728.84 \text{ Joule Ans.}$$

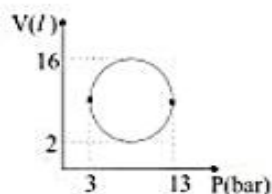
(iii)  $\Delta H_{AB} = C_p (T_2 - T_1) = \frac{5}{2} R \times 300 = 750 R = 6235.5 \text{ Joule}$  Ans.

$\Delta H_{BC} = 0$  Ans.

$\Delta H_{CD} = \Delta U_{CD} + nR \Delta T = n C_p \Delta T = 1 \times \frac{5}{2} R \times (-300) = -6235.5 \text{ Joule}$  Ans.

$\Delta H_{DA} = \Delta U_{DA} + nR \Delta T = 0 \text{ Joule}$  Ans.

**Q.16** Work done (in kJ) by the gas in the following cyclic process is



(A) -11

(B) -11000

(C) 11

(D) 11000

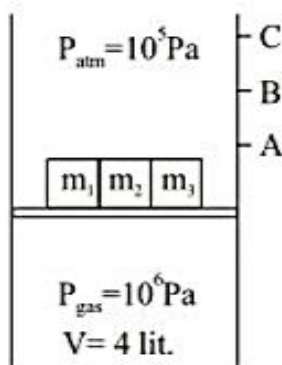
Ans. (A)

Sol.  $|w| = \pi ab = \frac{22}{7} \times 7 \times 5 = 110 \text{ bar lit.} = 11000 \text{ J} = 11 \text{ kJ}$

Final Answer = -11

**Q.17** Consider an isothermal cylinder and massless piston assembly in which ideal gas is filled. Cross sectional area of the cylinder =  $1 \text{ m}^2$ . Three masses  $m_1$ ,  $m_2$  and  $m_3$  are kept on the piston. When  $m_1$  is removed, piston moves upto point A. When  $m_1$  &  $m_2$  both are removed piston moves upto point B & when  $m_1$ ,  $m_2$  &  $m_3$  all the three are removed, piston moves upto point C. Calculate work done by the gas (in joule) when piston moves from point B to point C.

[Given :  $m_1 = 2 \times 10^4 \text{ kg}$ ,  $m_2 = 3 \times 10^4 \text{ kg}$ ,  $g = 10 \text{ m/s}^2$ ]



Sol. Initially piston is at eq,

$$10^6 = \frac{(2 \times 10^4 + 3 \times 10^4 + m_3) \times 10}{1} + 10^5$$

$$m_3 = \left( \frac{10^6 - 10^5}{10} \right) - 5 \times 10^4 = 10^4 (10 - 1) - 5 \times 10^4 = 10^4 (9 - 5) = 4 \times 10^4 \text{ kg}$$

since  $T = \text{constant}$

$$P_i V_i = P_B V_B$$

$$10^6 \times 4 = (10^5 + 4 \times 10^5) \times V_B$$

$$V_B = \frac{4 \times 10^6}{10^5 \times 5} = \frac{40}{5} = 8 \text{ lit.}$$

Also,

$$P_B V_B = P_C V_C$$

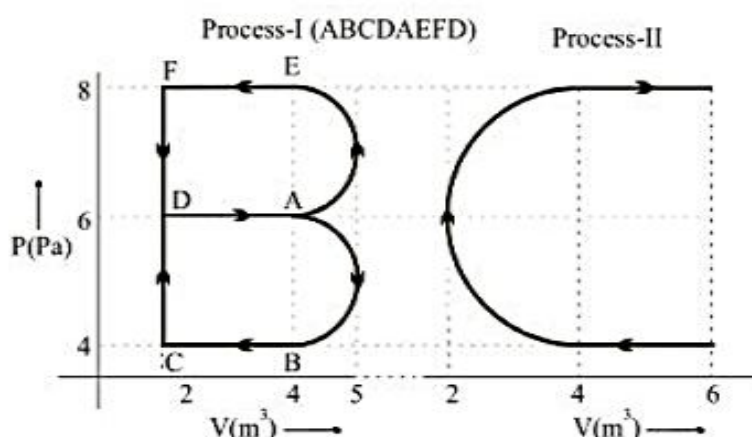
$$10^5 \times 5 \times 8 = 10^5 \times V_C$$

$$V_C = 40 \text{ L}$$

$$W_{BC} = -P_{\text{ext}}(V_C - V_B) = -10^5 (40 - 8) \times 10^{-3} = -3200 \text{ J}$$

$$W_{\text{by}} = 3200 \text{ J Ans.}$$

- Q.18** Calculate difference in work done in process-I to process-II.  
(Given :  $\pi = 3$ )



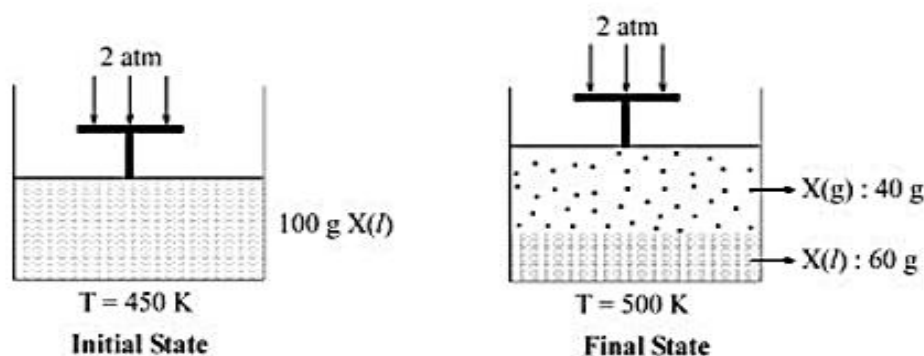
**Sol. Process-I :**  $W_{\text{ABCDAEFD}} = W_{\text{ABCD}} + W_{\text{AE}} + W_{\text{EF}} + W_{\text{FD}}$

$$= - \left( 2 \times 2 + \frac{3 \times 1 \times 1}{2} \right) + \frac{3 \times 1 \times 1}{2} + 8 \times 2 + 0 = -5.5 + \frac{3}{2} + 16 = 12$$

**Process-II :**  $w = \left( \frac{3 \times 2 \times 2}{2} + 4 \times 2 \right) = -(6 + 8) = -14$

Difference in work done =  $12 - (-14) = 26$  Ans.

- Q.19** The external pressure 2 atm is applied on frictionless movable piston, fitted in a vessel containing 100 g of X (l) at 450 K. Now heat is supplied keeping pressure constant till 40 g of X is evaporated to form X (g) at 500 K (boiling point). Calculate change in internal ( $\Delta U$ ) energy in kJ for overall process. Assume vapour of X (l) behaves like an ideal gas.





**Given:** Molar heat capacity of X ( $l$ ) =  $60 \text{ J/mol} \cdot \text{K}$  ;  $\Delta H_{\text{vaporisation}} = 30 \text{ kJ/mol}$  ;  $R = 8.3 \text{ J/mol} \cdot \text{K}$   
 At. weight of X =  $20 \text{ g/mol}$ .

**[Fill your answer by multiplying it with 100.]**

**Sol.**  $\Delta U = Q + w$

$$= n_{C_{pm}} \Delta T + n \Delta H_{\text{vap}} + w = \frac{100}{20} \times \frac{60}{1000} \times 50 + \frac{40}{20} \times 30 - \Delta n_g RT = 15 + 60 - \frac{2 \times 8.3 \times 500}{1000}$$

$$= 66.7 \text{ kJ} \quad \Rightarrow \quad 6670 \text{ Ans.}$$

**Q.20** An ideal gas with adiabatic exponent  $\gamma$  undergoes a process in which internal energy depends on volume as  $U = aV^\alpha$  then select the correct statement.

(A) Change in internal energy is  $\frac{(\gamma-1)}{\alpha} \Delta T$

(B) Molar heat capacity of process is  $\frac{R}{(1-\gamma)} + \frac{R}{\alpha}$

(C) Heat exchange in the process is given by  $\Delta U \left[ 1 + \frac{(1-\gamma)}{\alpha} \right]$

(D) Equation of process is  $PV^x = \text{constant}$ , where  $x > 0$  if  $\alpha < 1$ .

**Ans. (D)**

**Sol.**  $U = aV^\alpha \quad \Rightarrow \quad nC_v T = aV^\alpha$

$$TV^{-\alpha} = a$$

On comparing with  $TV^{n-1} = \text{constant}$

Polytropic index,  $n = 1 - \alpha$

$$\text{Molar heat capacity, } = \frac{R}{\gamma-1} - \frac{R}{n-1} = -\frac{R}{1-\gamma} + \frac{R}{1-(1-\alpha)} = -\frac{R}{1-\gamma} + \frac{R}{\alpha}$$

$$q = C \Delta T$$

$$= \left[ -C_v + \frac{R}{\alpha} \right] \Delta T = -C_v \Delta T + \frac{R}{\alpha} \Delta T = -\Delta U + \frac{R}{\alpha} \Delta T; \quad = -\Delta U + \frac{\gamma-1}{\gamma-1} \times \frac{R \Delta T}{\alpha}$$

$$= -\Delta U + \frac{R}{\gamma-1} \Delta T \times \frac{\gamma-1}{\alpha}; \quad = -\Delta U + \Delta U \cdot \frac{\gamma-1}{\alpha} = \Delta U \left[ \frac{\gamma-1}{\alpha} - 1 \right]$$

**Q.21** An adiabatic cylinder fitted with an adiabatic piston at the right end of cylinder, is divided into two equal halves with a monoatomic gas on left side and diatomic gas on right side, using an impermeable movable

adiabatic wall. If the piston is pushed slowly to compress the diatomic gas to  $\frac{3}{4}$ th of its original volume.

The new volume of monoatomic gas would be

(A)  $V_{\text{new}} = V_{\text{initial}} \times \left[ \frac{4}{3} \right]^{\frac{25}{21}}$

(B)  $V_{\text{new}} = V_{\text{initial}} \times \left[ \frac{7}{5} \right]^{\frac{3}{4}}$

(C)  $V_{\text{new}} = V_{\text{initial}} \times \left[ \frac{3}{4} \right]^{\frac{21}{25}}$

(D)  $V_{\text{new}} = V_{\text{initial}} \times \frac{3}{4}$

Ans. (C)

Sol.  $PV^\gamma = K$   
for diatomic gas

$$\frac{P_1}{P_2} = \left( \frac{V_2}{V_1} \right)^\gamma = \left( \frac{3}{4} \right)^{7/5}$$

for monoatomic gas

$$\frac{P_1}{P_2} = \left( \frac{V_{\text{new}}}{V_{\text{initial}}} \right)^{5/3} = \left( \frac{3}{4} \right)^{7/5} \Rightarrow V_{\text{new}} = V_{\text{initial}} \times \left[ \frac{3}{4} \right]^{\frac{21}{25}}$$

**Q.22** Calculate the work done by system in an irreversible (single step) adiabatic expansion of 1 mole of a polyatomic gas from 300K and pressure 10 atm to 1 atm. ( $\gamma = 1.33$ ).

Sol.  $C_v(T_2 - 300) = -1 \left( \frac{RT_2}{1} - \frac{RT_1}{10} \right)$

$$\gamma = 1.33 = \frac{4}{3} = \frac{C_p}{C_v} = \left( \frac{4}{3} \right) \quad C_p = C_v + R$$

$$3R(T_2 - 300) = -RT_2 + \frac{RT_1}{10}$$

$$4RT_2 = 30R + 900R$$

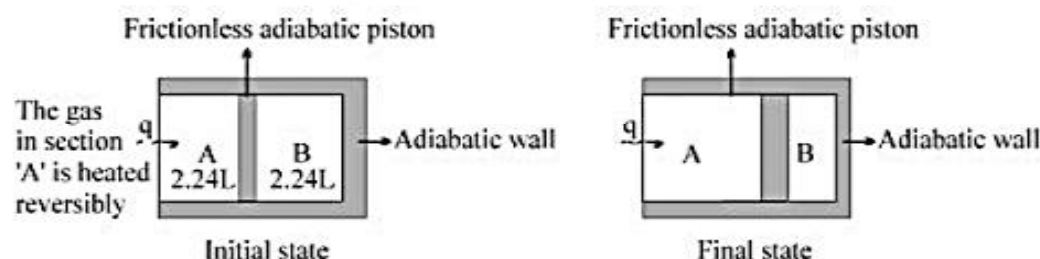
$$T_2 = \frac{930}{4} = 232.5 \text{ K}$$

$$W = 3R(232.5 - 300)$$

$$W = -202.5 R = -1.683 \text{ kJ}$$

**Q.23** A cylindrical container of volume 4.48 litres is containing equal no. of moles of a monoatomic gas in two sections A and B separated by an adiabatic frictionless piston as shown in figure. The initial temperature and pressure of gases was 273 K and 1 atm. Now gas in section 'A' is slowly heated till the volume of section B becomes  $1/2\sqrt{2}$  of initial volume. Find total change in  $\Delta H$  for section A and B. (in cal/mole)

[ $C_v$  of monoatomic gas =  $3/2 R$ ,  $\gamma = 5/3$ ]



[Use  $R = 2 \text{ cal/mol}$  &  $\sqrt{2} = 1.4$ ]

Sol. Initial volume of sec. A = sec. B = 2.24 litres

$$\text{Final volume of sec. B} = \left[ \frac{2.24}{2\sqrt{2}} \right] \text{ litres}$$

The gas in sec. 'B' compressed reversibly and adiabatically

$$\Rightarrow T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1} \Rightarrow T_2 = T_1 \left( \frac{V_1}{V_2} \right)^{\gamma-1} \Rightarrow T_2 = T_1 (2\sqrt{2})^{2/3} = 2T_1$$

{For monoatom gas  $\gamma = \frac{5}{3}$ }

The final pressure in sec. 'B'

$$P_f = \frac{P_1 V_1}{T_1} \cdot \frac{T_2}{V_2} = P_1 \times \left( \frac{T_2}{T_1} \right) \cdot \left( \frac{V_1}{V_2} \right) = P_1 \times 2 \times 2\sqrt{2} = 4\sqrt{2} \text{ atm}$$

$$\Rightarrow \text{Pressure in sec. 'A'} = 4\sqrt{2} \text{ atm} \quad \Rightarrow \text{Final temperature in sec. A } T_2 = \left( \frac{P_2}{P_1} \right) \left( \frac{V_2}{V_1} \right) T_1$$

$$T_2 = \left( \frac{P_2}{P_1} \right) \left\{ \frac{V_1 + V_1 - \frac{V_1}{2\sqrt{2}}}{V_1} \right\} T_1$$

$$4\sqrt{2} \left( 2 - \frac{1}{2\sqrt{2}} \right) T_1 = \left[ \frac{(4\sqrt{2}-1)(4\sqrt{2})}{2\sqrt{2}} \right] T_1$$

$$(4\sqrt{2}-1) 2T_1$$

$$[8\sqrt{2} T_1 - 2T_1 - T_1] = \{4\sqrt{2} T_1 - 3T_1\}$$

$$\Delta H_A = (0.1) \frac{5}{2} R \{8\sqrt{2} - 3\} \Rightarrow \Delta H_B = (0.1) \frac{5}{2} R \{273\}$$

$$2(4\sqrt{2}-1)$$

$$\Delta H_T = (0.1) \frac{5}{2} R (273) \{2\} (4\sqrt{2}-1) = 1255.8 \text{ or } 5 \times 1255.8 = 6279 \text{ Ans.}$$

- Q.24** A gas ( $C_{v,m} = \frac{5}{2} R$ ) behaving ideally was allowed to expand reversibly and adiabatically from 1 litre to 32 litre. Its initial temperature was  $327^\circ\text{C}$ . The molar enthalpy change (in J/mole) for the process is  
 (A) -1125 R (B) -575 R (C) -1575 R (D) None of these

**Ans.** (C)

**Sol.**  $\frac{T_2}{T_1} = \left( \frac{V_1}{V_2} \right)^{\gamma-1} \Rightarrow T_2 = T_1 \cdot \left( \frac{1}{32} \right)^{\frac{7}{5}-1} = 600 \cdot \left( \frac{1}{2^5} \right)^{\frac{2}{5}} = 600(0.5)^2 = 150\text{K}$

$$\Delta H_m = \frac{7}{2} R \times (150 - 600) = -1575 R \quad \text{Ans.}$$



**Q.25** 1000 gm water is heated from 27°C to 47°C at a constant pressure of 1 bar. The coefficient of volume expansion of water is 0.002/°C and the molar volume of water at 0°C is 18.00 cm<sup>3</sup>/mol. The magnitude of work done (in J) by water is

**Sol.**  $V_{t^{\circ}\text{C}} = V_{0^{\circ}\text{C}} (1 + \gamma t)$   $\gamma = \text{coefficient of volume expansion}$

$$V_{27^{\circ}\text{C}} = 1000 (1 + 0.002 \times 27) \quad t = \text{temperature in } ^{\circ}\text{C}$$

$$= 1054 \text{ ml}$$

$$V_{47^{\circ}\text{C}} = 1000 (1 + 0.002 \times 47)$$

$$= 1094 \text{ ml}$$

$$W = -P\Delta V = \frac{-1 \times (1094 - 1054)}{1000} \text{ bar litre} = \frac{-4}{100} \text{ bar litre} = \frac{-4}{100} \times 100 \text{ J} = -4 \text{ J}$$

**Q.26** The temperature of a definite amount of an ideal monoatomic gas becomes four times in a reversible process for which heat exchange is zero. Which of the following is correct relation between the final and initial parameters of gas?

(A)  $V_f = 8V_i$       (B)  $P_f = 32P_i$       (C)  $V_f = 16V_i$       (D)  $P_f = \frac{1}{16}P_i$

**Ans. (B)**

**Sol.**  $\left(\frac{V_1}{V_2}\right) = \left(\frac{T_2}{T_1}\right)^{\frac{1}{\gamma-1}} = (3)^{3/2} = 8$

$$\frac{P_1}{P_2} = \left(\frac{T_2}{T_1}\right)^{\frac{\gamma}{1-\gamma}} = (3)^{\frac{5/3}{-2/3}} = (3)^{-5/2} = \frac{1}{32}$$

**Q.27** Inversion temperature  $\left(T_i = \frac{2a}{Rb}\right)$  is defined as the temperature above which if gas is expanded adiabatically it gets warm up but if temperature of gas is lower than  $T_i$  then it will cool down. What will happen to a gas if it is adiabatically expanded at 50°C if its Boyle's temperature is 20°C

(A) heating      (B) cooling      (C) constant      (D) None of these

**Ans. (B)**

**Sol.** Boyle temperature,  $T_b = \frac{a}{Rb} = 20^{\circ}\text{C} = 293 \text{ K}$

inversion temperature,  $T_i = \frac{2a}{Rb} = 586 \text{ K} = 313^{\circ}\text{C}$

$\therefore$  at  $50^{\circ}\text{C} < T_i$ , on expansion cooling occurs

**Q.28** Which of the following statement(s) is/are correct :

Statement (a): The entropy of isolated system with P-V work only is always maximized at equilibrium

Statement (b): It is possible for the entropy of close system to decrease substantially in an irreversible process.

Statement (c): Entropy can be created but not destroyed.

Statement (d):  $\Delta S_{\text{system}}$  is always zero for reversible process in an isolated system

(A) Statement a, b, c      (B) Statement b, d      (C) Statement a, b, d      (D) All

**Ans. (D)**



- Q.29** 1 Kg stone at 27 °C falls 100 m into a lake whose temperature is 27 °C. Find the entropy change of  
 (a) the stone (b) the lake (c) the universe when  
 (i) stone is lowered reversibly  
 (ii) stone is dropped freely  
 Compare the loss of available energy in two cases

**Sol.(i)** If the stone is lowered reversibly no amount of heat will be produced. Also since temp of stone remains the same

$$\Delta S_{\text{stone}} = 0 \quad \text{Ans.};$$

$$q_{\text{rev}} = 0 \Rightarrow \Delta S_{\text{lake}} = 0 \quad \text{Ans.}$$

$$\text{and } \Delta S_{\text{total}} = \Delta S_{\text{universe}} = \Delta S_{\text{lake}} + \Delta S_{\text{stone}} = 0 \quad \text{Ans.}$$

- (ii)** If the stone is lowered irreversibly, the potential energy will be entirely lost in form of heat energy

$$q_{\text{actual}} = q_{\text{irr}} = mgh$$

$$\Delta S_{\text{stone}} = 0 \quad \text{Ans.}$$

$$\Delta S_{\text{lake}} = -\frac{q_{\text{irr}}}{T} = -\left(\frac{-1 \times 9.8 \times 1000}{300}\right) = \frac{980}{300} \text{ J/K}$$

$$= 3.26 \text{ J/K} \quad \text{Ans.}$$

$$\Delta S_{\text{total}} = 3.26 \text{ J/K} \quad \text{Ans.}$$

loss of available energy in first process = 0

loss of available energy in second process = 980 Joules

- Q.30** A mole of steam is condensed at 100°C, the water is cooled to 0°C and frozen to ice. What is the difference in entropies of the steam and ice? The heats of vaporization and fusion are 540 cal gm<sup>-1</sup> and 80 cal gm<sup>-1</sup> respectively. Use the average heat capacity of liquid water as 1 cal gm<sup>-1</sup> degree<sup>-1</sup>.

$$(A) 18 \left( \frac{80}{373} + \frac{540}{273} + \ln \frac{373}{273} \right)$$

$$(B) 18 \left( \frac{80}{273} + \frac{540}{373} + \ln \frac{373}{273} \right)$$

$$(C) 18 \left( \frac{80}{273} + \frac{540}{373} + \ln \frac{273}{373} \right)$$

$$(D) 18 \left( \frac{80}{273} + \frac{540}{373} + 100 \right)$$

**Ans. (B)**

**Sol.**  $\Delta S_{\text{condensation}} = \frac{-\Delta H_{\text{vap}}}{T} = \frac{-540 \times 18}{373}$

$$\Delta S_{\text{cooling}} = +nC_p \ln \left( \frac{T_2}{T_1} \right) = 18 \ln \left( \frac{273}{373} \right)$$

$$\Delta S_{\text{fusion}} = \frac{-80 \times 18}{273}$$

$$= - \left[ 18 \left( \frac{80}{273} + \frac{540}{373} \right) + \left( 18 \ln \frac{273}{373} \right) \right]$$

$$= -18 \left( \frac{80}{273} + \frac{540}{373} + \ln \frac{373}{273} \right) \Rightarrow 36.95 \text{ cal /}^\circ \quad \text{Ans.}$$

- Q.31** Heat capacity of a solid A(s), is given by  $aT^3$  in vicinity at absolute zero. Taking heat capacity to be  $aT^3$  from 0 K to 10 K,  $b$  from 10 K to normal M.P. at 150 K and  $c$  from 150 K to 200 K, find the absolute entropy of A (l) at 200 K.

Given  $a = 0.5 \times 10^{-3} \text{ J/(K mole)}$

$b = 15 \text{ J/(K mole)}$

$c = 20 \text{ J/(K mole)}$

$\Delta H_{\text{fusion}} = +30 \text{ KJ/mole}$

**Sol.** 
$$S_T - S_{0\text{K}} = \int_{0\text{K}}^{10\text{K}} \frac{C(s).dT}{T} + \int_{10}^{150\text{K}} \frac{C(s).dT}{T} + \frac{\Delta H_{\text{fusion}}}{T_M} + \int_{150}^{200} \frac{C(l).dT}{T}$$

$$S_T = \int_{0\text{K}}^{10\text{K}} \frac{aT^3.dT}{T} + \int_{10}^{150} \frac{b.dT}{T} + \frac{\Delta H_{\text{fusion}}}{T_M} + \int_{150}^{200} \frac{C.dT}{T}$$

$$S_T = a \left[ \frac{10^3}{3} - 0 \right] + b \ln \left( \frac{150}{10} \right) + \frac{30000}{150} + c \ln \left( \frac{200}{150} \right)$$

$$S_T = \frac{0.5}{3} + 15 \times \ln(15) + 200 + 20 \ln \frac{4}{3}$$

$$S_T = 0.166 + 40.62 + 200 + 5.8$$

$$S_T = 246.586 \text{ J / (mole. K) Ans.}$$

- Q.32** For a perfectly crystalline solid  $C_{p,m} = aT^3 + bT$ , where  $a$  &  $b$  are constant. If  $C_{p,m}$  is 0.40 J/K-mol at 10 K and 0.92 J/K-mol at 20 K, then molar entropy at 20 K is

(A) 0.92 J/K-mol (B) 8.66 J/K-mol (C) 0.813 J/K-mol (D) None

**Ans. (C)**

**Sol.**  $0.40 = aT_1^3 + bT_1 \Rightarrow 0.40 = a \times (1000) + b \times 10$

$$\Rightarrow 0.4 = 1000a + 10b \quad \dots(1)$$

$$0.92 = aT_2^3 + bT_2 \Rightarrow 0.92 = a \times 8000 + 20b \quad \dots(2)$$

On solving

$$0.12 = 6000a \quad ; \quad a = 2 \times 10^{-5}$$

$$0.40 = 2 \times 10^{-5} \times 1000 + b \times 10$$

$$\therefore b = 0.038$$

$$S_m = \int \frac{aT^3 + bT}{T} .dT \Rightarrow \frac{a[T_2^3 - T_1^3]}{3} + b[T_2 - T_1]$$

$$\Rightarrow \frac{2 \times 10^{-5} \times (8000 - 0)}{3} + b(20) \Rightarrow \frac{2 \times 10^{-5} \times 8000}{3} + 0.038 \times (20)$$

$$\Rightarrow 0.053 + 0.76 \Rightarrow 0.813 \text{ J/K-mol}$$

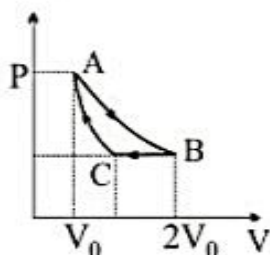
- Q.33** Two mole of an ideal gas is expanded irreversibly & isothermally at  $27^\circ\text{C}$  until its volume is doubled and 3.3 kJ heat is absorbed from surrounding. Determine  $\Delta S_{\text{system}}$  &  $\Delta S_{\text{surrounding}}$ .

**Sol.**  $\Delta S_{\text{system}} = nR \ln \frac{V_2}{V_1} \Rightarrow 2 \times R \times \ln 2 \Rightarrow 11.52 \text{ J/K}$

$$\Delta S_{\text{surrounding}} = -\frac{3.3 \times 1000}{300} \Rightarrow -11 \text{ J/K}$$

**Q.34** An ideal gas undergoing cyclic process ABCA consisting of isothermal expansion AB, isobaric compression BC & adiabatic compression CA. Find the % (approximate) efficiency of cycle.

[Given :  $T_A = T_B = 400 \text{ K}$  ;  $\gamma = 1.5$ ,  $\ln 2 = 0.7$ ,  $2^{-1/3} = 0.8$  ]



**Sol.**  $T_C = T_A \left[ \frac{P_A}{P_C} \right]^{\frac{1-\gamma}{\gamma}} = 400 \left[ \frac{2}{1} \right]^{\frac{1-1.5}{1.5}} = \frac{400}{2^{1/3}} = 400 \times 0.8 = 320$

$$\eta = - \frac{W_{\text{Total}}}{q_{\text{absorbed}}}$$

$$W_{AB} = -nR T \ln 2 = -280 nR$$

$$W_{BC} = -nR (T_C - T_B) = -nR (320 - 400) = 80 nR$$

$$W_{CA} = \frac{nR}{\gamma - 1} (T_A - T_C) \\ = 2 nR (400 - 320) \\ = 160 nR$$

$$W_{\text{total}} = -280 nR + 80 nR + 160 nR \\ = -40 nR$$

$$q_{\text{adsorbed}} = -W_{AB} \\ = 280 nR$$

$$\% \eta = \frac{40 nR}{280 nR} \times 100 = \frac{100}{7} = 14.285 \approx 14 \text{ Ans.}$$

**Q.35** 0.5 mole of an ideal monoatomic gas at STP conditions undergoes a process, if the final volume of gas is  $(22.7 \times e)$  lit., then the entropy change in this process in J / K / mol is

[Given : Process isobaric]

(Fill your answer by multiplying it with  $\frac{100}{R}$  )

**Sol.**  $\frac{V_1}{V_2} = \frac{T_1}{T_2} \Rightarrow \frac{22.7/2}{22.7.e} = \frac{273}{T_2} \Rightarrow T_2 = 273. (2e)$

$$\Delta S = nC_p \ln \frac{T_2}{T_1} = 0.5 \times \frac{5}{2} R \times \ln \frac{(273).(2e)}{(273)}$$

$$= \frac{5}{4} R (\ln 2e) = \frac{5}{4} R (\ln 2 + \ln e) \quad \therefore \text{if } \ln 2 = 0.7$$

$$= \frac{5}{4} R \times (1.7) \times \frac{100}{R} = 212.5 \text{ Ans.}$$



**Q.36** When two equal sized pieces of the same metal at different temperatures  $T_h$  (hot piece) and  $T_c$  (cold piece) are brought into contact into thermal contact and isolated from it's surrounding. The total change in entropy of system is given by

(A)  $C_v \ln \frac{T_c + T_h}{2T_c}$       (B)  $C_v \ln \frac{T_2}{T_1}$       (C)  $C_v \ln \frac{(T_c + T_h)^2}{2T_h \cdot T_c}$       (D)  $C_v \ln \frac{(T_c + T_h)^2}{4T_h \cdot T_c}$

**Ans. (D)**

**Sol.**  $C_v(T_h - T) = C_v(T - T_c) \Rightarrow T = \frac{T_c + T_h}{2}$  ;  $\therefore \Delta S = \int_{T_1}^{T_2} \frac{C_v \cdot dt}{T}$

$$\Delta S_c = C_v \ln \frac{T}{T_c} \text{ \& \; } \Delta S_h = C_v \ln \frac{T}{T_h}$$

$$\text{Total } \Delta S = C_v \ln \frac{(T_c + T_h)}{2T_c} + C_v \ln \frac{(T_c + T_h)}{2T_h} = C_v \ln \frac{(T_c + T_h)^2}{4T_c \cdot T_h}$$

**Q.37** A reversible heat engine A (based on carnot cycle) absorbs heat from a reservoir at 1000K and rejects heat to a reservoir at  $T_2$ . A second reversible engine B absorbs, the same amount of heat as rejected by the engine A, from the reservoir at  $T_2$  and rejects energy to a reservoir at 360K.

If the efficiencies of engines A and B are the same then the temperature  $T_2$  is

(A) 680 K      (B) 640 K      (C) 600 K      (D) none

**Ans. (C)**

**Sol.** For heat engine A:  $\eta_A = \frac{1000 - T_2}{1000} \Rightarrow \eta_B = \frac{T_2 - 360}{T_2}$

$$\eta_A = \eta_B$$

$$\text{so } \frac{1000 - T_2}{1000} = \frac{T_2 - 360}{T_2} = T_2 = \sqrt{360 \times 1000} = 600 \text{ K Ans.}$$

**Q.38** Which of the following statement(s) is/are correct:

Statement (a): In any closed system with P, V work only, G is always minimized at equilibrium.

Statement (b):  $\Delta G$  is always zero for a reversible process in a closed system.

Statement (c):  $\Delta G^\circ$  for an ideal gas reaction is a function of pressure.

Statement (d): For an irreversible, isothermal, isobaric process in a closed system with P, V work only.  $\Delta G$  must be negative.

(A) Statement a, b, d    (B) Statement b, c, d    (C) Statement c, d    (D) Only statement d

**Ans. (D)**

**Q.39** Select the correct statement(s).

(A)  $dG = Vdp - SdT$  is applicable for all process involving both 'PV' and 'non-PV' work in a closed system.

(B)  $\Delta S_{\text{sys}}$  can not be negative in any adiabatic process in a closed system.

(C)  $\Delta U = 0$  for the combustion of  $C_6H_6(g)$  in a sealed rigid diathermic container.

(D) In the presence of 'non-PV' work if  $(\Delta G_{\text{sys}})_{T,P} < 0$ , process must be spontaneous in a closed system.

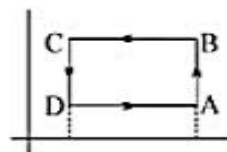
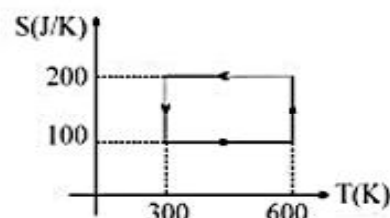
**Ans. (B)**



- Sol. (A)**  $G = H - TS = U + PV - TS$   
 $dG = dU + PdV + VdP - TdS - SdT$   
 $= q + w + PdV + VdP - TdS - SdT$   
 For a reversible path  $q = TdS$   
 If there is no non-PV work  $w = -PdV$   
 $dG = VdP - SdT$
- (D)**  $G = H - TS = U + PV - TS$   
 at constant 'T' & 'P'  
 $dG_{sys} = dU + PdV - TdS_{sys} = q + w_{PV} + w_{non-PV} + PdV - TdS_{sys}$   
 since  $w_{PV} = -PdV$   
 and in the absence of  $w_{non-PV}$   
 $dG_{sys} = q - TdS_{sys}$   
 $dG_{sys} = -T(dS_{sys} + dS_{surr})$

**Q.40** From the given T-S diagram of a reversible carnot engine, find

- (i) work delivered by engine in one cycle  
 (ii) heat taken from the source in each cycle.  
 (iii)  $\Delta S_{sink}$  in each cycle.



**Sol.(i)**  $W_{AB} = -nRT \ln \frac{V_2}{V_1}$

$$\Delta S = \frac{q_{rev}}{T} = -\frac{W_{AB}}{T}$$

$$\Rightarrow -W_{AB} = T\Delta S = 600 \times 100$$

$$-W_{BC} = -nC_V(T_1 - T_2)$$

$$-W_{CD} = T\Delta S = 300 \times (-100)$$

$$-W_{DA} = -nC_V(T_2 - T_1)$$

$$\text{net work delivered during one cycle} = -W_{AB} - W_{BC} - W_{CD} - W_{DA} = 300 \times 100 = 30 \text{ kJ}$$

**Note :** Net work done = area of the rectangle

**(ii)**  $\frac{W_{net}}{q} = \eta$  and  $\eta = \frac{600 - 300}{600} = \frac{1}{2}$

$$\Rightarrow q = \text{heat taken from the source} = \frac{-W_{net}}{1/2} = \frac{30 \text{ kJ}}{1/2} = +60 \text{ kJ}$$

**(iii)**  $\Delta S_{sink} = -\frac{q_{sink}}{T}$  also  $(q_{source} + q_{sink}) = 30$

$$q_{source} = 60 \Rightarrow q_{sink} = -30 \text{ kJ}$$

$$\Rightarrow \Delta S_{sink} = \frac{-q_{sink}}{T} = \frac{-(-30000 \text{ J})}{100} = 100 \text{ J/K} \quad \text{Ans.}$$

**Q.41** Fixed amount of an ideal gas contained in a sealed rigid vessel ( $V = 24.6$  litre) at 1.0 bar is heated reversibly from  $27^\circ\text{C}$  to  $127^\circ\text{C}$ . Determine change in Gibb's energy ( $|\Delta G|$  in Joule) if entropy of gas  $S = 10 + 10^{-2} T$  (J/K)

**Sol.**  $dG = V.dP - S.dT$  ; at const. volume

$$\Delta G = V.\Delta P - \int (10 + 10^{-2} T).dT \quad \frac{P_1}{T_1} = \frac{P_2}{T_2} \Rightarrow P_2 = 1 \times 400/300$$

$$\Delta G = 24.6 \times \left( \frac{4}{3} - 1 \right) \times 100 - \left[ 10 \times 100 + 10^{-2} \times \left( \frac{T_2^2}{2} - \frac{T_1^2}{2} \right) \right]$$

$$\Delta G = 24.6 \times \frac{1}{3} \times 100 - \left[ 1000 + 10^{-2} \times \left( \frac{160000}{2} - \frac{90000}{2} \right) \right]$$

$$= 24.6 \times \frac{1}{3} \times 100 - 1000 - 350 = -530 \text{ J}$$

**Q.42** A reaction at 300 K with  $\Delta G^\circ = -1743 \text{ J/mol}$  consists of 3 mole of A (g), 6 mole of B (g) and 3 mole of C (g). If A, B and C are in equilibrium in 1 litre container then the reaction may be

[Given :  $2 = e^{0.7}$ ,  $R = 8.3 \text{ J/K - mol}$ ]

(A)  $A + B \rightleftharpoons C$  (B)  $A \rightleftharpoons B + 2C$  (C)  $2A \rightleftharpoons B + C$  (D)  $A + B \rightleftharpoons 2C$

**Ans.** (C)

**Sol.**  $\Delta G^\circ = -RT \ln K_{eq}$

$$\text{or, } -1743 = -8.3 \times 300 \times \ln k_{eq}$$

$k_{eq} = 2 = k_{eq}$  for reaction  $2A \rightleftharpoons B + C$  from given data.

## THERMOCHEMISTRY

Thermochemistry is the study of the energy and heat associated with chemical reactions and/or physical transformations. Thermochemistry coalesces the concepts of thermodynamics with the concept of energy in the form of chemical bonds. The subject commonly includes calculations of such quantities as heat capacity, heat of combustion, heat of formation, enthalpy.

A reaction may release or absorb energy, and a phase change may do the same, such as in melting and boiling. Thermochemistry focuses on these energy changes, particularly on the system's energy exchange with its surroundings.

### ENTHALPY

Chemical reactions are generally carried out at constant pressure (atmospheric pressure) so it has been found useful to define a new state function **Enthalpy** ( $H$ ) (earlier defined in thermodynamics) :

$$H = U + PV$$

and hence,  $\Delta H = \Delta U + \Delta(PV)$

At constant pressure

$$\Delta H = \Delta U + P \Delta V$$

Combining with first law,

$$\Delta H = q_p$$

Hence, transfer of heat at constant pressure brings about a change in the enthalpy of the system.

### Enthalpy change, $\Delta_r H$ of a reaction-Reaction enthalpy-Heat of reaction

The enthalpy change accompanying a reaction is called the reaction enthalpy. It may also be defined as the amount of heat lost or gained in the chemical reaction, when all the reactants and products are maintained at the same temperature and pressure. The enthalpy change of a chemical reaction may be given as

$$\begin{aligned}\Delta_r H &= (\text{sum of enthalpies of products}) - (\text{sum of enthalpy of reactants}) \\ &= \sum (\nu_p H)_{\text{products}} - \sum (\nu_p H)_{\text{reactants}}\end{aligned}$$

where  $\nu$  is the stoichiometric coefficients of reactants and products, respectively.

### Types of Reactions :

- (i) **Exothermic Reactions** : Heat is evolved during the reaction. For such reactions  $\Delta_r H$  is negative, which implies that

$$\sum \nu_p H (\text{products}) < \sum \nu_R H (\text{reactants})$$

- (ii) **Endothermic Reactions** : Heat is absorbed during the reaction. For such reactions  $\Delta_r H$  is positive, which implies that

$$\sum \nu_p H (\text{products}) > \sum \nu_R H (\text{reactants})$$



**Note :**

1. For a reaction whose  $\Delta H = +ve$  and  $\Delta E = -ve$ , what will be the classification as exothermic and endothermic.
2. In general, reactions have  $\Delta H$  and  $\Delta E$  of same sign unless the values of  $\Delta H$  and  $\Delta E$  are exceptionally small

**Factors affecting  $\Delta H$  of the reactions are :**

- (i) Physical states of reactants & products
  - (ii) Allotropic forms of elements
  - (iii) Reaction conditions (constant pressure or constant volume)
- (i) Condition of constant P or V : Heat changes at constant volume are expressed as  $\Delta E$   
Heat changes at constant pressure are expressed as  $\Delta H$   
Also for a change  $\Delta H = \Delta E + P\Delta V$  .....(1)  
where P is the pressure and  $\Delta V$  is change in volume.

Also  $\Delta H$  and  $\Delta E$  are related together as

$$\Delta H = \Delta E + \Delta n_g RT \quad \text{.....(2)}$$

Where  $\Delta H$  and  $\Delta E$  are change in enthalpy and change in internal energy for a given change respectively.

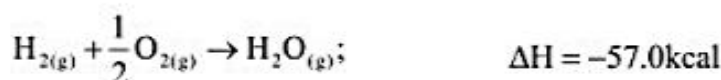
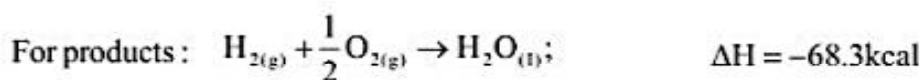
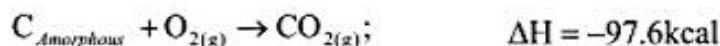
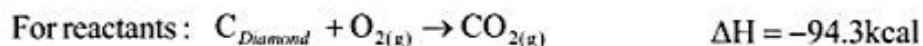
$\Delta n_g$  = Moles of gaseous products - Moles of gaseous reactants.

R = Molar gas constant

T = Temperature in Kelvin

**NOTE :** While using eq. (2) for numerical one should keep in mind that for

- a. For calculation of  $\Delta n_g$  only gaseous moles of reactants and products are considered
  - b. If  $\Delta n_g = 0$ ;  $\Delta H = \Delta E$
  - c.  $\Delta n_g$  may be +ve or -ve integer or fraction.
  - d. Put R in the same units in which  $\Delta H$  and  $\Delta E$  are given.
  - e. Normally reactions are carried out at constant pressure and therefore, heat changes are to be taken as  $\Delta H$  unless stated otherwise.
- (ii) Physical nature of reactants and products :



Therefore, it is necessary to write physical state of reactants and products while writing thermochemical equation.

- (iii) Temperature : The variation of  $\Delta H$  or  $\Delta E$  with temperature is expressed in terms of Kirchhoff's equation as,  $\Delta H_2 - \Delta H_1 = \Delta C_p(T_2 - T_1)$  or  $\Delta E_2 - \Delta E_1 = \Delta C_v(T_2 - T_1)$



Where  $\Delta H$  and  $\Delta E$  are heats of reaction at temperature  $T_1$

$\Delta H_1$  and  $\Delta E_1$  are heats of reaction at temperature  $T_2$

$$\Delta C_p = \sum \nu_p C_{p(\text{Product})} - \sum \nu_p C_{p(\text{Reactant})}$$

$$\Delta C_v = \sum \nu_p C_{v(\text{Product})} - \sum \nu_p C_{v(\text{Reactant})}$$

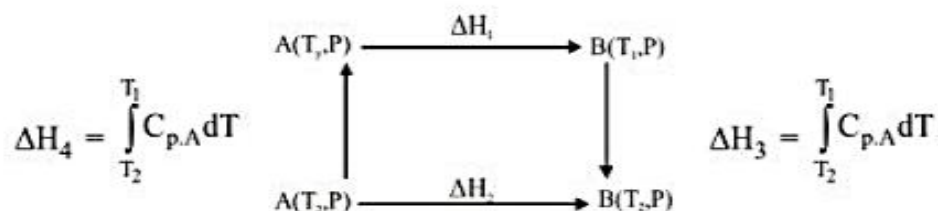
$C_p$  and  $C_v$  are molar specific heats at constant  $P$  and  $V$  respectively.

**Note :**

1. The above expression should be used only when all the gases involved are ideal and reaction occurs at constant temperature.
2. It is advisable to start with  $\Delta H = \Delta E + \Delta(PV)$  which is a general expression and then depending upon data appropriate expressions should be used.

**Variation of enthalpy with temperature (Kirchoff's Equation) :-** The enthalpy of chemical reactions and phase transition do vary with temperature. Although the variation in  $\Delta H$  with temperature is usually small compared to the value of  $\Delta H$  itself.

consider a reaction  $A \rightarrow B$  at temperature  $T_1$  and pressure  $P$



**Since  $H$  is state function :-** Change in enthalpy in cyclic process is equal to zero. To calculate enthalpy change ( $\Delta H_2$ ) at temperature  $T_2$  at constant pressure consider cyclic process shown in figure. It is clear  $\Delta H_3$  = change in enthalpy of  $A$  when temperature is raised from  $T_1$  to  $T_2$  at constant

pressure.  $\Delta H_3 = \int_{T_1}^{T_2} C_{p,A} dT$

$\Delta H_4$  = Change in enthalpy taking 1 mole of  $B$  at constant pressure from  $T_1$  to  $T_2$

$$\Delta H_4 = \int_{T_1}^{T_2} C_{p,B} dT \quad \text{now :}$$

$$\Delta H_3 + \Delta H_1 + \Delta H_4 = \Delta H_2$$

$$\Rightarrow \Delta H_2 - \Delta H_1 = \Delta H_3 + \Delta H_4 \quad \Rightarrow \Delta H_2 - \Delta H_1 = \int_{T_1}^{T_2} (C_{p,B} - C_{p,A}) dT$$

$$\Rightarrow \Delta H_2 - \Delta H_1 = \Delta_r C_p (T_2 - T_1)$$

If  $\Delta_r C_p$  is independent of 'temperature'

**Standard enthalpy of Reaction,  $\Delta_r H^\circ$  :**

As enthalpy of a reaction depends on the conditions under which a reaction is carried out, it is necessary to specify some standard conditions. The standard enthalpy of reaction is the enthalpy change for a reaction, when all the participating substance (reactants and products) are in their standard condition.

**Note :**1. **The standard condition are :**

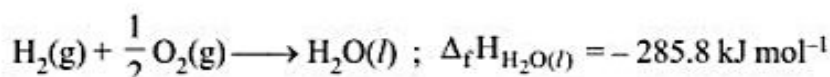
\* Solid / liquid / gas should be at 1 bar

\* For substance dissolved in solution concentration should be 1M.

## 2. Standard conditions in Thermodynamics does not specify any temperature. However in Electrochemistry it is taken as 298K.

**Enthalpy changes in chemical reactions :****(1) Enthalpy of Formation,  $\Delta_f H$  :**

It is the enthalpy change when one mole of a substance is formed from its elements in their most abundant naturally occurring form (also called reference states).

**Note :**1. By convention, enthalpy of formation  $\Delta_f H$ , of an element in reference state is taken as zero.

2. The enthalpy of formation can be used to determine the enthalpy change of any reaction as

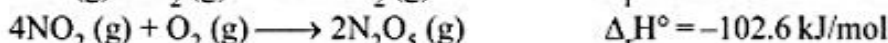
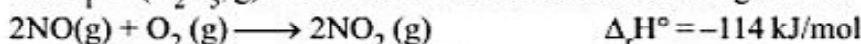
$$\Delta_r H = \sum_i a_i \Delta_f H_{(\text{Products})} - \sum_i b_i \Delta_f H_{(\text{reactants})}$$

where  $a_i$  and  $b_i$  represent the coefficients of the products and reactants in the balanced chemical equation.

3.  $\Delta_f H$  data can be used to compare stability of isomer and allotropes

4. The reference state of commonly used elements are :

Elements	Reference state
C	C <sub>(graphite)</sub>
S	S <sub>8(Rhombic)</sub>
P	P <sub>4(white)</sub>
O	O <sub>2(g)</sub>
H	H <sub>2(g)</sub>
Br	Br <sub>2(l)</sub>
Metal	M <sub>(s)</sub> [except Hg <sub>(l)</sub> ]
P	P <sub>4(white)</sub>

**Illustration**1. The  $\Delta_f H^\circ$  ( $N_2O_5$ , g) in kJ/mol on the basic of the following data is :

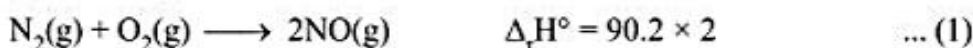
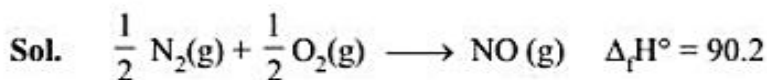
$$\Delta_f H^\circ (NO, g) = 90.2 \text{ kJ/mol}$$

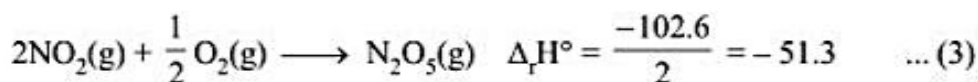
(A) 15.1

(B) 30.2

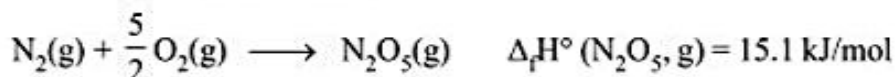
(C) -36.2

(D) None of these

**Ans. (A)**



Addition of (1), (2) and (3) equation



### Exercise

1. How much heat will be required at constant pressure to form 1.28 kg of  $\text{CaC}_2$  from  $\text{CaO}(\text{s})$  &  $\text{C}(\text{s})$ ?

Given:  $\Delta_f H^\circ (\text{CaO}, \text{s}) = -152 \text{ kcal/mol}$ .

$\Delta_f H^\circ (\text{CaC}_2, \text{s}) = -14 \text{ kcal/mol}$

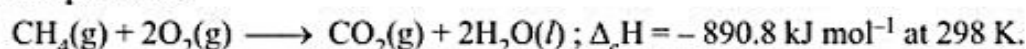
$\Delta_f H^\circ (\text{CO}, \text{g}) = -26 \text{ kcal/mol}$

(A) +112 kcal      (B) 224 kcal      (C) 3840 kcal      (D) 2240 kcal

Ans. (D)

### (2) Enthalpy of Combustion, $\Delta_c H$ :

It is the enthalpy change when one mole of the substance undergo complete combustion to give combustion products.



The combustion products of the substances are

Elements	Combustion products
C	$\text{CO}_{2(\text{graphite})}$
H	$\text{H}_2\text{O}_{(\text{l})}$ or $\text{H}_2\text{O}_{(\text{g})}$ [depends on condition]
S	$\text{SO}_{2(\text{g})}$

### Illustration

1. The heat of combustion of sucrose,  $\text{C}_{12}\text{H}_{22}\text{O}_{11}(\text{s})$  at constant volume is  $-1348.9 \text{ kcal mol}^{-1}$  at  $25^\circ\text{C}$ , then the heat of reaction at constant pressure, when stem is produced, is

Sol. The combustion equation of sucrose is



Here,

$\Delta n_g = \text{sum of gaseous product moles} - \text{sum of gaseous reactant moles}$

$\Delta n_g = 11$

$\Delta H = \Delta E + \Delta n_g RT$ ,

Here,  $\Delta E = -1348.9 \text{ kcal}$

$R = 2.0 \text{ cal}, T = 25 + 273 = 298 \text{ K}$

$\therefore \Delta H = (-1348.9 \times 1000) + 11 \times 2 \times 298$

$= -1348900 + 6556 = -1342344 \text{ cal}$

$= -1342.344 \text{ kcal}$



---

**Exercise**


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1. For the given heat of reaction,  
 (i)  $\text{C(s)} + \text{O}_2(\text{g}) = \text{CO}_2(\text{g}) + 97 \text{ kcal}$       (ii)  $\text{CO}_2(\text{g}) + \text{C(s)} = 2\text{CO(g)} - 39 \text{ kcal}$   
 the heat of combustion of  $\text{CO(g)}$  is :

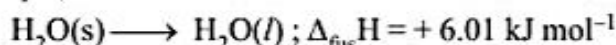
**Ans.** 69 kcal

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**(3) Enthalpy changes during phase transformations :**

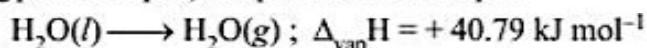
- (i) **Enthalpy of Fusion,  $\Delta_{\text{fus}} H$  :** It is the enthalpy change that accompanies melting of one mole of a solid substance at constant temperature (melting point of solid) and pressure.

for example,



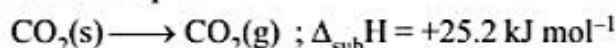
- (ii) **Enthalpy of Vaporisation,  $\Delta_{\text{vap}} H$  :**

It is the enthalpy change required to vapourise one mole of a liquid substance at constant temperature (boiling point of liquid) and pressure for example :



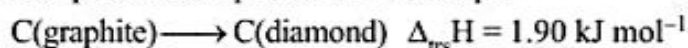
- (iii) **Enthalpy of Sublimation,  $\Delta_{\text{sub}} H$  :**

It is the enthalpy change required to sublime one mole of a solid substance at constant temperature and pressure. For example



- (iv) **Enthalpy of Transition :**

It is the enthalpy change when one mole of one allotropic form changes to another under conditions of constant temperature and pressure. For example

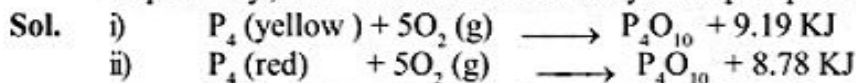



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**Illustration**


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1. The heats of combustion of yellow phosphorus and red phosphorous are - 9.19 KJ and - 8.78 KJ respectively, then heat of transition of yellow phosphorus to red phosphorous is



Subtracting,  $\text{P}_4(\text{yellow}) - \text{P}_4(\text{red}) = 1.13 \text{ KJ}$

$\Rightarrow \text{P}_4(\text{yellow}) = \text{P}_4(\text{red}) + 1.13 \text{ KJ}$

So, heat of transition of yellow to red phosphorus is - 1.13 KJ

---

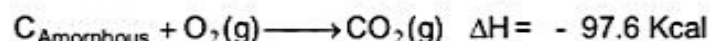


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**Exercise**


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1. The heat of transition for carbon from the following



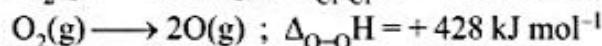
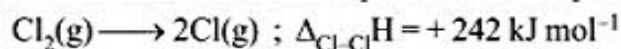
**Ans.** 3.3 KJ/mol

---



**(4) Bond Enthalpies (Bond energies),  $\Delta_{\text{bond}} H$  :**

The bond enthalpy of diatomic molecules like  $H_2$ ,  $Cl_2$ ,  $O_2$  etc. may be defined as the enthalpy change when one mole of covalent bonds of a gaseous covalent substance is broken to form products in the gas phase, under conditions of constant pressure and temperature. For example



In case of polyatomic molecules, bond dissociation enthalpy is different for different bonds within the same molecule. In such cases, mean bond enthalpy is used. Mean bond enthalpy may be defined as the average enthalpy change to dissociate a particular type of bond in the compounds.

In gas phase reactions, the standard enthalpy of reaction,  $\Delta_r H^\circ$ , is related with the bond enthalpies of reactants and products as

$$\Delta_r H^\circ = \Sigma \text{ bond enthalpies (reactants)} - \Sigma \text{ bond enthalpies (products)}$$

$$= \Sigma \epsilon \text{ of reactants} - \Sigma \epsilon \text{ of products}$$

**Illustration**

1. For the reaction



Calculate the bond enthalpy of  $N=N$ .

Given : B.E. ( $N-N$ ) = 163 kJ/mol, B.E. ( $N-H$ ) = 391 kJ/mol, B.E. ( $H-H$ ) = 436 kJ/mol

- Sol.** The equation :

$$\Delta H = 109 = \epsilon_{N-N} + 4\epsilon_{N-H} - \epsilon_{H-H} - 2\epsilon_{N-H} - \epsilon_{N=N}$$

$$\epsilon_{N=N} = 163 + 2 \times 391 - 436 - 109 = 400 \text{ kJ/mole}$$

**Exercise**

1. What is the Bond energy (In kJ/mol) of  $C-H$  in Methane from the following data?

$$\Delta H_f [CO_2(g)] = - 394 \text{ kJ / mol}$$

$$\Delta H_f [H_2O(l)] = - 285 \text{ kJ / mol}$$

$$\Delta H_{\text{sublimation}} \{\text{Carbon (graphite)}\} = + 716 \text{ kJ/mol}$$

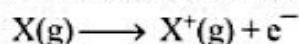
$$\Delta H_{\text{combustion}} [CH_4(g)] = - 890 \text{ kJ / mol}$$

$$\text{Bond energy (H-H)} = 435 \text{ kJ/mol}$$

**Ans.** 415 kJ/mol

**(5) Ionisation Enthalpy ( $\Delta_i H$ )**

It is the enthalpy change when an electron is removed from an isolated gaseous atom or in its ground state under conditions of constant temperature and pressure.

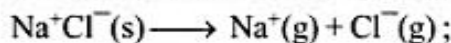
**(6) Electron Gain Enthalpy ( $\Delta_{eg} H$ )**

It is the enthalpy change when an electron is added to a neutral gaseous atom to convert it into a negative ion under conditions of constant temperature and pressure.



**(7) Lattice Enthalpy ( $\Delta_{\text{lattice}} H$ )**

The lattice enthalpy of an ionic compound is the enthalpy change which occurs when one mole of an ionic compound dissociates into its ions in gaseous state under conditions of constant temperature and pressure.

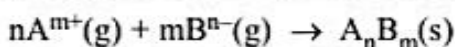


$$\Delta_{\text{lattice}} H = + 788 \text{ kJ mol}^{-1}$$

Lattice enthalpy can also be defined for the reverse process. In that case the value of  $\Delta H_{\text{LE}}$  will be negative.

**Born–Haber Cycle For NaCl :**

This cycle is based on thermochemical changes taking place in the formation of a lattice. This cycle can be used to determine lattice energy which cannot be directly measured. It is defined as that energy released when one mole of the ionic compound (lattice) is formed its isolated ions in the gaseous state under standard condition.



$$\Delta H = - U \text{ (lattice energy)}$$

Formation of NaCl(s) lattice involves thus.

$$S + I + \frac{\epsilon_{\text{Cl-Cl}}}{2} - E - U = q$$

hence,  $U$  can be calculated.

here,  $S$  = enthalpy of sublimation of Na(s) =  $\Delta H_{\text{sublimation}}$

$I$  = ionisation of energy of Na(g) =  $\Delta H_{\text{ionization}}$

$\epsilon$  = bond energy of  $\text{Cl}_2$

$U$  = lattice energy

$q$  = enthalpy of formation of NaCl(s) =  $\Delta H_{\text{formation}}$

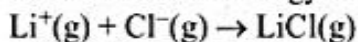
If lattice is  $\text{MgX}_2(\text{s})$  then

$$S + (I_1 + I_2) + \epsilon - 2E - U = q$$

where,  $(I_1 + I_2)$  = total ionisation energy to form  $\text{Mg}^{2+}(\text{g})$ .

**Illustration**

1. Calculate lattice energy for the change,



Given that

$\Delta H_{\text{sublimation}}$  of Li =  $160.67 \text{ kJ mol}^{-1}$ ,

$\Delta H_{\text{ionisation}}$  of Li(g) =  $520.07 \text{ kJ mol}^{-1}$ ,

$\Delta H_f$  of LiCl(s) =  $- 401.66 \text{ kJ mol}^{-1}$ .

$\Delta H_{\text{Dissociation}}$  of  $\text{Cl}_2$  =  $244.34 \text{ kJ mol}^{-1}$ ,

$\Delta H_{\text{E.A}}$  of Cl(g) =  $- 365.26 \text{ kJ mol}^{-1}$ ,

- Sol. Considering the different changes that occur in the formation of solid lithium chloride based on the data given the lattice energy of the above can be constituted as :

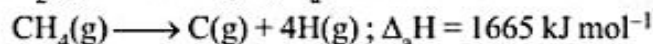
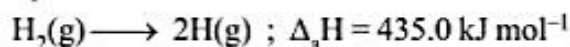
$$\Delta H_f^\circ = \Delta H_{\text{subl.}} + \Delta H_{\text{I.E.}} + \frac{1}{2} \Delta H_{\text{Diss.}} + \Delta H_{\text{E.A}} + \Delta H_{\text{lattice}}$$

$$\begin{aligned} \text{or } \Delta H_{\text{lattice}} &= \Delta H_f^\circ - \Delta H_{\text{subl.}} - \Delta H_{\text{I.E.}} - \frac{1}{2} \Delta H_{\text{Diss.}} - \Delta H_{\text{E.A}} \\ &= - 839.31 \text{ kJ mol}^{-1} \end{aligned}$$

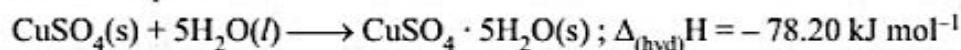
**(8) Enthalpy of Atomisation,  $\Delta_a H$  :**

It is the enthalpy change when one mole of a substance is completely dissociated into atoms in the gaseous state, under constant pressure and temperature condition.

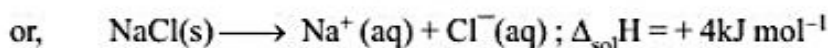
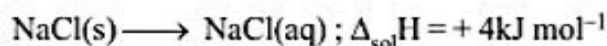
For example

**(9) Enthalpy of Hydration,  $\Delta_{\text{hyd}} H$  :**

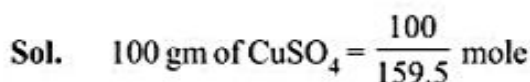
It is the enthalpy change when one mole of an anhydrous (or partly hydrated) compound combines with the required number of moles of water to form a specific hydrate at the specified temperature and pressure. For example :

**(10) Enthalpy of Solution,  $\Delta_{\text{sol}} H$  :**

It is the enthalpy change when one mole of a substance is dissolved in a specified amount of solvent under conditions of constant temperature and pressure. When large volume of solvent is taken, the enthalpy change is called enthalpy of solution at infinite dilution. For example

**Illustration**

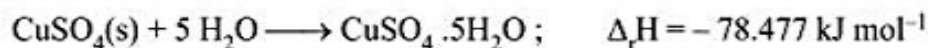
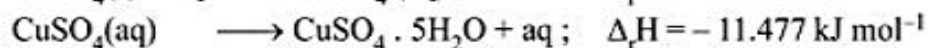
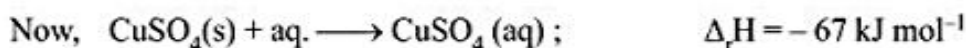
1. 100 gm of anhydrous  $\text{CuSO}_4$ , when dissolved in excess of water produces 42 kJ of heat. The same amount of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  on dissolving in large excess of water absorbed 4.60 kJ. What is the heat of hydration  $\text{CuSO}_4$ ?



$$\text{Heat of solution of } \text{CuSO}_4 \text{ per mole} = -\frac{42 \times 159.5}{100} = -66.99 \text{ kJ} \Rightarrow -67 \text{ kJ}$$

$$100 \text{ gm of } \text{CuSO}_4 \cdot 5\text{H}_2\text{O} = \frac{100}{249.5} \text{ mole}$$

$$\text{Heat of solution per mole (} \text{CuSO}_4 \cdot 5\text{H}_2\text{O}) = 4.6 \times \frac{249.5}{100} = 11.477 \text{ kJ}$$

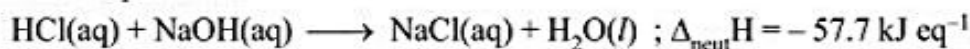


$\therefore$  Enthalpy of hydration of  $\text{CuSO}_4(\text{s}) ; \Delta H = -78.477 \text{ kJ mol}^{-1}$  **Ans.**



**(11) Enthalpy of Neutralisation  $\Delta_{\text{neut}}H$  :**

It is the enthalpy change when one g-equivalent of an acid and one g-equivalent of a base undergo complete neutralisation in aqueous solution and all the reactants & products are at the same specified temperature and pressure.

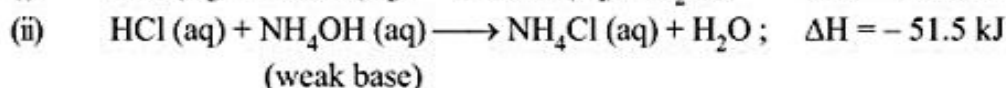
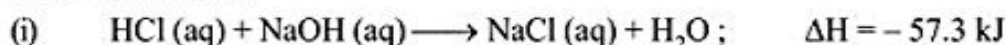


The enthalpy of neutralisation of strong acid and strong base is always constant ( $-57.7 \text{ kJ eq}^{-1}$ ), independent from the acid and base taken. However, the magnitude of enthalpy change of neutralisation decreases when any one of the acid or base taken is weak.

The value ( $-57.7 \text{ kJ eq}^{-1}$ ) is the value when acids and bases are taken in their infinitely diluted state. If acids and bases are having some other concentration, then value will differ.

**Illustration**

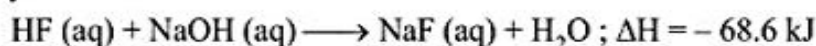
1. Heat of neutralization ( $\Delta H$ ) of  $\text{NH}_4\text{OH}$  and  $\text{HF}$  are  $-51.5$  and  $-68.6 \text{ kJ}$  respectively. Calculate their heat of dissociation?



**Sol.**  $\therefore$  The heat of dissociation of  $\text{NH}_4\text{OH}$ ,

$$\Delta H = -51.5 - (-57.3) = 5.8 \text{ kJ}$$

Similarly we have



$\therefore$  The heat of dissociation of  $\text{HF}$ ,

$$\Delta H = -68.6 - (-57.3) = -11.3 \text{ kJ}$$

**Exercise**

1. Calculate  $\Delta_{\text{neut}}H$  of  $\text{HA}$ . If bond dissociation energy of  $\text{H-A}$  is  $5 \text{ KJ/mol}$

**Ans.**  $-52.7 \text{ KJ/mol}$

**(12) Resonance energy :**

When two or more double bond are in conjugation, there is possibility of delocalization of electron through conjugation. The Phenomenon is called resonance. Due to resonance, the molecule gain stability. The actual structure of molecule is average of many possible canonical structure possible for molecule. When ever there is possibility of Resonance energy is difference in energy of most stable canonical structure and energy of actual molecule.

When ever there is possibility of resonance in molecule, the molecule become more stable and bond breaking become difficult.



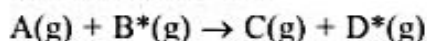
### Calculation of resonance energy using bond energy :

Resonance energy can be calculated using the formula

$$\Delta H (\text{Actual}) - \Delta H (\text{theoretical}) = \text{resonance energy of products} - \text{Resonance energy of reactants}$$

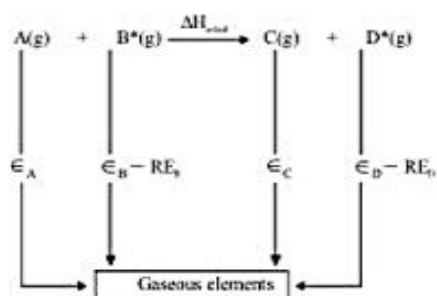
The proof of above formula is given by following diagram.

Consider a reaction



where (\*) showing that molecules exhibit phenomena of resonance. Remember where ever resonance take place, bond breaking become difficult.

Actual energy required to break a bond is equal to  $\epsilon_{\text{actual}} = \epsilon_{\text{theoretical}} - \text{resonance energy}$



$$\Delta H_{\text{actual}} = \epsilon_A + \epsilon_B - R.E_B - \{\epsilon_C + \epsilon_D - R.E_D\}$$

$$\Delta H_{\text{actual}} = (\epsilon_A + \epsilon_B - \epsilon_C - \epsilon_D) + R.E_B - R.E_D$$

$$[\Delta H_{\text{actual}} - \Delta H_{\text{Theoretical}} = R.E_{\text{Products}} - R.E_{\text{reactants}}]$$

**Note :** The value of resonance energy may be positive or negative, but assign it's sign on the basis that resonance always increases the stability and decreases the energy of molecule. Due to resonance in a molecule, bond breaking become difficult hence actual energy required to break a bond = theoretical bond energy – resonance energy.

### Illustration

1. Calculate resonance energy of  $C_6H_6(g)$ .

Given:  $\Delta H_f [C_6H_6(g)] = -360 \text{ kJ mol}^{-1}$

$$\Delta H_{\text{Sub}} [C(\text{graphite})] = 716 \text{ kJ mol}^{-1}$$

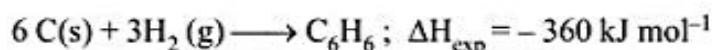
$$B.E_{H-H} = 437 \text{ kJ mol}^{-1}$$

$$B.E_{C-C} = 620 \text{ kJ mol}^{-1}$$

$$B.E_{C-C} = 340 \text{ kJ mol}^{-1}$$

$$B.E_{C-H} = 490 \text{ kJ mol}^{-1}$$

**Sol.** For  $C_6H_6$



$$\begin{aligned} \therefore \Delta H_{\text{cal}} &= -[3(C-C) + 3(C=C) + 6(C-H)] + [6C_{s \rightarrow g} + 3(H-H)] \\ &= -[3 \times 340 + 3 \times 620 + 6 \times 490] + [6 \times 716 + 3 \times 437] \\ &= -5820 + 5607 = -213 \text{ kJ mol}^{-1} \end{aligned}$$

$$\begin{aligned} \therefore \text{Resonance energy} &= \text{Exp. } \Delta H_f - \text{Calculated } \Delta H_f \\ &= -360 - (-213) = -360 + 213 = -147 \text{ kJ mol}^{-1} \end{aligned}$$

## Exercise

1. The standard molar enthalpies of formation of cyclohexane (*l*) and benzene (*l*) at 25°C are –156 and +49 kJ mol<sup>-1</sup> respectively. The standard enthalpy of hydrogenation of cyclohexene (*l*) at 25°C is –119 kJ mol<sup>-1</sup>. Use these data to estimate the magnitude of the resonance energy of benzene.

Ans. 152 KJ

**Different types of standard enthalpy changes (Based on IUPAC recommendations) :**

	Transition Enthalpy	Example	Definition	Symbol
1.	Enthalpy of formation	$\text{K(s)} + \frac{1}{2} \text{Cl}_2(\text{g}) \rightarrow \text{KCl(s)}$	One mole of the compound formed from its elements	$\Delta_f H^\circ$ or $\Delta H^\circ_f$
2.	Enthalpy of combustion	$\text{C}_2\text{H}_6(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\ell)$	One mole of the compound (fuel) is burnt completely in oxygen	$\Delta_c H^\circ$ or $\Delta H^\circ_c$
3.	Enthalpy of fusion	$\text{H}_2\text{O(s)} \rightarrow \text{H}_2\text{O(l)}$	One mole of the liquid is formed from the solid without a change in temperature	$\Delta_{\text{fus}} H^\circ$ or $\Delta H^\circ_{\text{fus}}$
4.	Enthalpy of vaporisation	$\text{H}_2\text{O(l)} \rightarrow \text{H}_2\text{O(g)}$	One mole of the vapour formed from the liquid without a change in temperature	$\Delta_{\text{vap}} H^\circ$ or $\Delta H^\circ_{\text{vap}}$
5.	Enthalpy of sublimation	$\text{I}_2(\text{s)} \rightarrow \text{I}_2(\text{g)}$	One mole of the vapour formed from the solid	$\Delta_{\text{sub}} H^\circ$ or $\Delta H^\circ_{\text{sub}}$
6.	Enthalpy of atomisation	$\text{H}_2(\text{g}) \rightarrow 2\text{H(g)}$	One mole of the substance broken into isolated atoms in the gas phases	$\Delta_{\text{at}} H^\circ$ or $\Delta H^\circ_{\text{at}}$
7.	Enthalpy of reaction	$\text{A} \rightarrow \text{B}$	Enthalpy change taking place in a reaction	$\Delta_r H^\circ$ or $\Delta H^\circ_r$

8.	Enthalpy of neutralisation	$\text{HCl(aq)} + \text{NaOH(aq)} \rightarrow \text{H}_2\text{O} + \text{NaCl(aq)}$	One mole of water formed by the neutralisation of an acid by a base	$\Delta_n H^\circ$ or $\Delta H_n^\circ$
9.	Enthalpy of ionisation	$\text{Na(g)} \rightarrow \text{Na}^+(\text{g}) + \text{e}^-$	One mole atoms ionised—all species in gaseous phase	$\Delta_{\text{ion}} H^\circ$ or $\Delta H_{\text{ion}}^\circ$
10.	Electron-gain enthalpy	$\text{X(g)} \rightarrow \text{e}^- \rightarrow \text{X}^-(\text{g})$	One mole of anions being formed all species in the gaseous phase	$\Delta_{\text{eg}} H^\circ$ or $\Delta H_{\text{eg}}^\circ$
11.	Lattice enthalpy	$\text{NaCl(s)} \rightarrow \text{Na}^+(\text{g}) + \text{Cl}^-(\text{g})$	One mole of a crystal completely separated into isolated particles in the gaseous phase	$\Delta_L H^\circ$ or $\Delta H_L^\circ$ or $U$
12.	Bond dissociation enthalpy (bond A – B)	$\text{HCl(g)} \rightarrow \text{H(g)} + \text{Cl(g)}$	One mole of bonds broken – all produce in the gaseous phase	$\Delta H_{\text{A-B}}^\circ = \epsilon_{\text{A-B}}$
13.	Enthalpy of solution	$\text{NaCl(s)} + \text{H}_2\text{O(excess)} \rightarrow \text{NaCl(aq)}$	One mole of the solute dissolved in excess of solvent so that further dilution produces no enthalpy change	$\Delta_{\text{sol}} H^\circ$ or $\Delta H_{\text{sol}}^\circ$
14.	Enthalpy of hydration	$\text{X}^+(\text{g}) \rightarrow \text{X}^+(\text{aq})$	One mole of the ion in gaseous phase is hydrated	$\Delta_{\text{hyd}} H^\circ$ or $\Delta H_{\text{hyd}}^\circ$
15.	Enthalpy of mixing	pure substance $\rightarrow$ mixture	One mole each of the two or more substances is mixed	$\Delta_{\text{mix}} H^\circ$ or $\Delta H_{\text{mix}}^\circ$

## CALORIMETRY - MEASURING HEATS OF REACTIONS

All calorimetric techniques are based on the measurement of heat that may be generated (exothermic process), consumed (endothermic process) or simply dissipated by a sample. There are numerous methods to measure such heat. Any process that results in heat being generated and exchanged with the environment is a candidate for a calorimetric study.



A calorimeter is a device used to measure heat of reaction. In order to measure heats of reactions, we often enclose reactants in a calorimeter, initiate the reaction, and measure the temperature difference before and after the reaction. The temperature difference enables us to evaluate the heat released in the reaction.

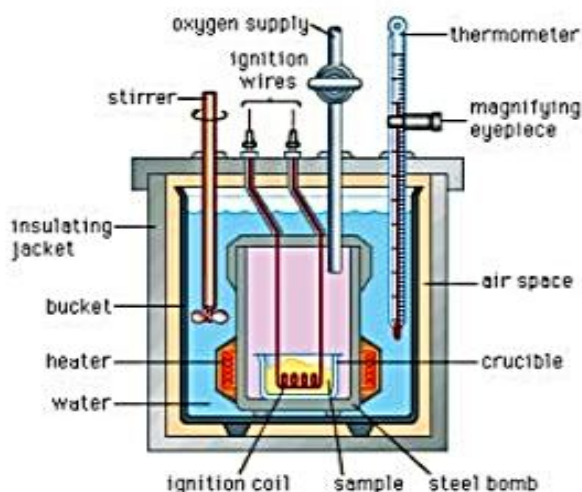
Two basic types of calorimetry are discussed :

- (a) measurement based on constant volume.
- (b) measurements based on constant pressure.

A calorimeter may be operated under constant volume which measures internal energy change  $\Delta U$  by bomb calorimeter or constant (atmosphere) pressure, which measures enthalpy change  $\Delta H$  by calorimeter. Whichever kind to use, heat capacity of the calorimeter is required.

The heat capacity is the amount of heat required to raise the temperature of the entire calorimeter by 1 K, and it is usually determined experimentally before or after the actual measurements of heat of reaction. The heat capacity of the calorimeter is determined by transferring a known amount of heat into it and measuring its temperature increase.

- (i) **Bomb calorimeter ( $\Delta U$  measurement) :** For chemical reactions, heat absorbed at constant volume, is measured in a bomb Calorimeter. In this Calorimeter, a steel vessel (the bomb) is immersed in a water bath. A combustible substance is burnt in pure oxygen supplied in the bomb. Heat evolved during the reaction is transferred to the water around the bomb and its temperature is monitored. Since the bomb Calorimeter is sealed, its volume does not change, i.e., the energy changes associated with reactions are measured at constant volume.



Since volume does not change, a bomb calorimeter measures the heat evolved under constant volume,

$$q_v,$$

$$q_v = C \Delta T,$$

where  $\Delta T$  is the temperature increase. The  $q_v$  so measured is also called the change in internal energy,  $\Delta E$ .

$$\Delta E = q_v = C \times \Delta T$$



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**Illustration**


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1. A calorimeter with heat capacity equivalent to having 13.3 moles of water is used to measure the heat of combustion from 0.303 g of sugar ( $C_{12}H_{22}O_{11}$ ). The temperature increase was found to be 5.0 K. Calculate the heat released, the amount of heat released by 1.0 g, and 1.0 mole of sugar.

Sol. Heat released,  $q_v$ ,

$$q_v = 13.3 \times 75.2 \times 5.0 \text{ K} \\ = 5000 \text{ J}$$

The amount of heat released by 1.0 g would be,

$$5000 \text{ J} / 0.303 \text{ g} = 16.5 \text{ kJ / g}$$

Since the molecular weight of sugar is 342 g/mol, the amount of heat released by 1.0 mole would be  $16.5 \times 342 = 5643 \text{ kJ/mol}$ .

2. The temperature of a calorimeter increases 0.10 K when 7.52 J of electric energy is used to heat it. What is the heat capacity of the calorimeter?

Sol. Dividing the amount of energy by the temperature increase yields the heat capacity,  $C$ ,  
 $C = 7.52 / 0.10 = 75.2 \text{ J/K}$ .

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**Exercise**


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1. The heat released by one mole of sugar from a bomb calorimeter experiment is 5648 kJ/mol. Calculate the enthalpy of combustion per mole of sugar.

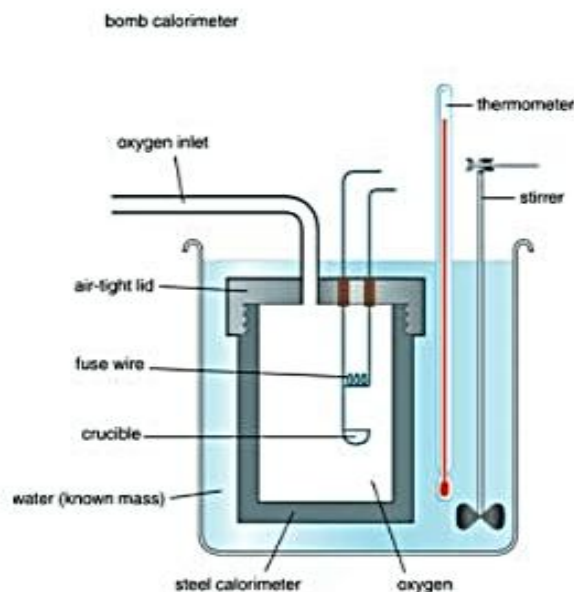
Ans. 5648 kJ/mol

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**Note:**

More heat is given off if the reaction is carried out at constant pressure, since the P-V work ( $1.5 RT$ ) due to the compression of 1.5 moles of gases in the reactants would contribute to  $dH$ . If 1.0 mole water is decomposed by electrolysis at constant pressure, we must supply an amount of energy equivalent to enthalpy change,  $dH$ , a little more than internal energy,  $dE$ . More energy must be supplied to perform the P-V work to be done by the products ( $H_2$  and  $O_2$ ).

- (ii)  **$\Delta H$  measurement** : Measurement of heat change at constant pressure (generally at atmospheric pressure) can be done in a Calorimeter shown in the figure. In this case, the Calorimeter is left open to atmosphere. As the reaction occurs in the Calorimeter, the temperature change is noticed and then heat of reaction is measured with the knowledge of heat capacity of Calorimeter system.

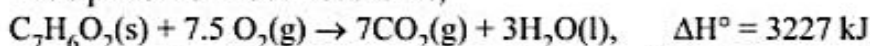


The heat capacity of the calorimeter can also be determined by burning an exactly known amount of a standard substance, whose enthalpy of combustion has been determined. Benzoic acid,  $C_7H_6O_2$ , is one such standard. The problem below illustrates the calculations.

### Illustration

- When 0.1025 g of benzoic acid was burnt in a bomb calorimeter the temperature of the calorimeter increased by  $2.165^\circ\text{C}$ . For benzoic acid  $\Delta H^\circ_{\text{comb}} = -3227\text{ kJ mol}^{-1}$ . Calculate the heat capacity of the calorimeter.

**Sol.** The equation for the combustion is,



Since 7.5 moles of  $O_2$  gas is needed, and 7 moles of  $CO_2$  is produced, some pressure-volume work is done, to the calorimeter:

$$P V = \Delta n_g R T, \text{ where } \Delta n = (7 - 7.5) = -0.5\text{ mol}$$

$$\Delta E = \Delta H - \Delta n_g R T$$

$$= -3227 - (-0.5 \times 8.314298 \times 298)$$

$$= -3226\text{ kJ/mol (a small correction)}$$

The amount of heat produced by 0.1025 g benzoic acid is

$$q = 0.1025/122.13 \times 3226 = 2.680\text{ kJ}$$

Thus, the heat capacity is

$$C = q_v / \Delta T = 2.680 / 2.165 = 1.238\text{ kJ / K}.$$

After the heat capacity is determined, the calorimeter is ready to be used to measure the enthalpy of combustion of other substances.

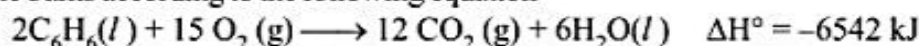
### Exercise

- When 0.7022 g of oxalic acid ( $C_2O_4H_2$ ) is burnt in the calorimeter. The temperature increased by  $1.602^\circ\text{C}$ . The heat capacity of the calorimeter is  $1.238\text{ kJ/K}$ . Calculate  $\Delta H^\circ_{\text{comb}}$ .

**Ans.**  $-250.6\text{ kJ/mol}$

## SOLVED EXAMPLE

**Q.1** Benzene burns according to the following equation



What is the  $\Delta E^\circ$  for the combustion of 1.5 mol of benzene

- (A)  $-3271 \text{ kJ}$       (B)  $-9813 \text{ kJ}$       (C)  $-4906.5 \text{ kJ}$       (D) None of these

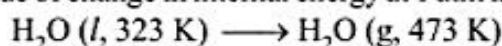
**Ans.** (D)

**Sol.**  $\Delta n = -3$

$$\Delta H^\circ = \Delta E^\circ + (\Delta n_g)RT$$

$$\Rightarrow -6542 = \Delta E^\circ + (-3)(8.31)(298) \times 10^{-3} \quad \Rightarrow \quad \Delta E^\circ = -6534 \text{ kJ}$$

**Q.2** What is the value of change in internal energy at 1 atm in the process

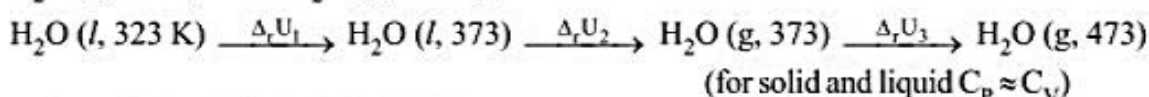


Given:  $C_{p(\text{H}_2\text{O}, l)} = 75.3 \text{ JK}^{-1} \text{ mol}^{-1}$ ;  $C_{p(\text{H}_2\text{O}, g)} = 33.314 \text{ JK}^{-1} \text{ mol}^{-1}$ ;  $\Delta H_{\text{vap}}$  at  $373 \text{ K} = 40.7 \text{ kJ/mol}$

- (A)  $109.1 \text{ kJ/mol}$       (B)  $37.6 \text{ kJ/mol}$       (C)  $43.86 \text{ kJ/mol}$       (D)  $48.36 \text{ kJ/mol}$

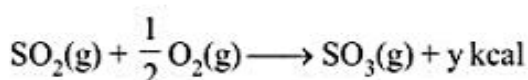
**Ans.** (C)

**Sol.**  $\text{H}_2\text{O}(l, 323 \text{ K}) \longrightarrow \text{H}_2\text{O}(g, 473 \text{ K})$



$$\begin{aligned} \text{and } \Delta_r U &= \Delta_r U_1 + \Delta_r U_2 + \Delta_r U_3 \\ &= C_{v,m} \Delta T + (\Delta_r H_2 - \Delta n_g RT) + C_{v,m} \Delta T \\ &= \frac{75.3 \times 50}{1000} + \left( 40.7 - \frac{1 \times 8.314 \times 398}{1000} \right) + \frac{(33.314 - 8.314) \times 100}{1000} \\ \Delta_r U &\approx 43.86 \text{ kJ/mol} \end{aligned}$$

**Q.3**  $\text{S}(s) + \frac{3}{2} \text{O}_2(g) \longrightarrow \text{SO}_3(g) + 2x \text{ kcal}$



Find out the heat of formation of  $\text{SO}_2(g)$

- (A)  $(y - 2x)$       (B)  $(2x + y)$       (C)  $(x + y)$       (D)  $2x/y$

**Ans.** (A)

**Q.4** The molar heat capacities at constant pressure (assumed constant with respect to temperature) of A, B and C are in ratio of **1.5 : 3.0 : 2.5**. If enthalpy change for the exothermic reaction  $\text{A} + 2\text{B} \longrightarrow 3\text{C}$  at  $300 \text{ K}$  and  $310 \text{ K}$  is  $\Delta H_1$  and  $\Delta H_2$  respectively then

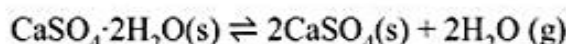
- (A)  $\Delta H_1 > \Delta H_2$   
 (B)  $\Delta H_1 < \Delta H_2$   
 (C)  $\Delta H_1 = \Delta H_2$   
 (D) If  $T_2 > T_1$  then  $\Delta H_2 > \Delta H_1$  & if  $T_2 < T_1$  then  $\Delta H_2 < \Delta H_1$

**Ans.** (C)

**Sol.**  $\Delta_r C_p = 3 \times 2.5 - 1 \times 1.5 - 2 \times 3 \Rightarrow 0$  ;  $\therefore \Delta H_1 = \Delta H_2$



- Q.5** Solid  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  is taken in a container fitted with a frictionless piston initially containing no other gases. The external pressure is maintained at 1 atm and the container is heated till the equilibrium is achieved.



If  $\Delta H^\circ = +30 \text{ Kcal/mol}$  and  $\Delta S^\circ = +40 \text{ cal/K}$ , at what temperature equilibrium will be established in the container. (Ignore variation of  $\Delta H^\circ$  and  $\Delta S^\circ$  with temperature.)

- (A) 600 K (B) 750 K (C) 700 K (D) 300 K

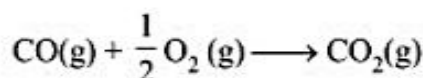
**Ans. (B)**

**Sol.** At Eq.  $\Delta G^\circ = 0$

$$\Delta H^\circ = T\Delta S^\circ$$

$$\Rightarrow T = \frac{\Delta H^\circ}{\Delta S^\circ} = 750 \text{ K}$$

- Q.6** For the reaction



using data given in table find out incorrect statement(s) among the following.

	$\Delta H_f^\circ (\text{kJ/mole})$	$S^\circ (\text{J/Kmole})$
$\text{CO}(\text{g})$	-110	+197
$\text{O}_2(\text{g})$	0	+205
$\text{CO}_2(\text{g})$	-395	+213

Assume vibration modes of motion do not contribute to heat capacity at low temperature.

(A)  $\Delta H^\circ > \Delta U^\circ$  for the reaction at 298K.

(B) In standard state condition, the reaction  $\text{CO}(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g})$  attain equilibrium at very high temperature.

(C) At low temperature  $\frac{d(\Delta H)^\circ}{dT} = -\text{ive}$

(D) In a  $\text{CO}$ ,  $\text{O}_2$  fuel cell electrical energy obtained by cell  $> |\Delta H_{\text{combustion}}^\circ [\text{CO}(\text{g})]|$

**Ans. (A)**

**Sol.**  $\Delta H^\circ - \Delta U^\circ = \Delta n_g RT$

since  $\Delta n_g = -\text{ve}$

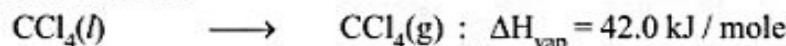
$$\Rightarrow \Delta H^\circ - \Delta U^\circ \leq 0$$

$$\Delta H^\circ = -\text{ve}$$

$$\Delta S^\circ = -\text{ve} \quad ; \quad C_p = \frac{3}{2}R + R \quad ; \quad = \frac{5}{2}R$$

$$\Delta_r C_p = -\text{ve}$$

- Q.7** The heat of vaporisation :  $\Delta H_{\text{vap}}$ , of  $\text{CCl}_4$  at  $27^\circ\text{C}$  is 42 kJ/mole



If 1 mole of liquid  $\text{CCl}_4$  at  $27^\circ\text{C}$  has entropy of 214 J/K mole, what is the entropy (in J/K-mol) of 1 mole of vapour in equilibrium with liquid at this temperature.

- (A) 74 (B) 454 (C) 354 (D) 254



Ans. (C)

Sol. If liquid  $\text{CCl}_4$  is in equilibrium with its vapour then

$$\frac{\Delta H_{\text{vap } 27^\circ\text{C}}}{300} = \Delta S_{\text{vap}} = S_{\text{CCl}_4(\text{g})} - S_{\text{CCl}_4(\text{l})}$$

$$\Rightarrow \frac{42,000}{300} = S_{\text{CCl}_4(\text{g})} - 214 \text{ J/K mole}$$

$$140 + 214 = 354 \text{ J/K mole}$$

Q.8 If  $\Delta H_{\text{vaporisation}}$  of substance X (l) (molar mass : 30 g/mol) is 300 J/g at its boiling point 300 K, then molar entropy change for reversible condensation process is

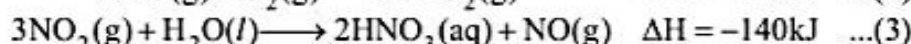
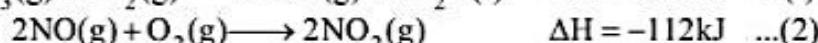
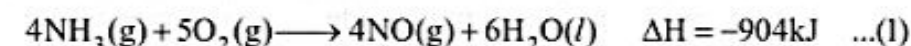
- (A) 30 J/mol.K (B) -300 J/mol.K (C) -30 J/mol.K (D) None of these

Ans. (C)

Sol.  $\Delta H_{\text{vaporisation}} = 300 \times 30 \text{ J/mol}$

$$\Delta S_{\text{condensation}} = \frac{-\Delta H_{\text{vaporisation}}}{T_{\text{boiling point}}} \Rightarrow \frac{-300 \times 30}{300} \text{ J/mol.K} \Rightarrow -30 \text{ J/mol.K} \quad \text{Ans.}$$

Q.9 The following sequence of reaction occurs in commercial production of aqueous nitric acid.



Determine the total heat liberated (in kJ/mol) at constant pressure for the production of exactly 1 mole of aqueous nitric acid from  $\text{NH}_3$  by this process.

- (A) 986 (B) 493 (C) 246.5 (D) None of these

Ans. (B)

Sol. 1 mole of  $\text{HNO}_3 = \frac{3}{2}$  moles of  $\text{NO}_2 \longrightarrow \frac{3}{2}$  mole of  $\text{NO} \longrightarrow \frac{3}{2}$  mole of  $\text{NH}_3$

$$-\left(\frac{3}{2} \times \frac{1}{4}\right)(904) - \left(\frac{3}{2} \times \frac{1}{2}\right)(112) - \left(\frac{3}{2} \times \frac{1}{3}\right)(140) = 493 \text{ kJ/mol}$$

Heat liberated = 493 kJ/mol

Q.10 If  $\Delta H_{\text{vaporisation}}$  of  $(\text{C}_2\text{H}_5)_2\text{O}$  (l) is 350 J/g at its boiling point 300 K, then molar entropy change for condensation process is

- (A) 86.33 J/mol.K (B) -86.33 J/mol.K (C) -1.16 J/mol.K (D) 1.16

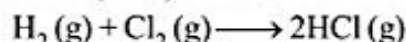
Ans. (B)

Sol.  $\Delta H_{\text{vaporisation}} = 350 \times 74 \text{ J/mol}$

$$\Delta S_{\text{condensation}} = \frac{-\Delta H_{\text{vaporisation}}}{T_{\text{boiling point}}}$$

$$= \frac{-350 \times 74}{300} \text{ J/mol.K} = -86.33 \text{ J/mol.K} \quad \text{Ans.}$$

**Q.11** Calculate  $\Delta G$  (in kJ) for the reaction at 300 K,



**Given at 300 K:**  $\text{BE}_{\text{H-H}} = 435 \text{ kJ mol}^{-1}$ ,  $\text{BE}_{\text{Cl-Cl}} = 240 \text{ kJ mol}^{-1}$ ,  $\text{BE}_{\text{HCl}} = 430 \text{ kJ mol}^{-1}$

Entropies of  $\text{H}_2$ ,  $\text{Cl}_2$  and  $\text{HCl}$  are 131, 223 and  $187 \text{ JK}^{-1} \text{ mol}^{-1}$  respectively.

- (A) 191 (B) 291 (C) -191 (D) None of these

**Ans.** (C)

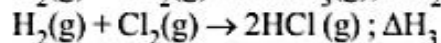
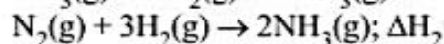
**Sol.**  $\Delta H = (435 + 240 - 2 \times 430) = -185 \text{ kJ mol}^{-1}$

$$\Delta S = \frac{2 \times 187 - (131 + 223)}{1000} = \frac{20}{1000} \text{ kJ mol}^{-1}$$

$$\Delta G = \Delta H - T\Delta S$$

$$= -185 - \frac{300 \times 20}{1000} = -185 - 6 = -191 \text{ kJ mol}^{-1}$$

**Q.12**  $\text{NH}_3(\text{g}) + 3\text{Cl}_2(\text{g}) \rightarrow \text{NCl}_3(\text{g}) + 3\text{HCl}(\text{g}); -\Delta H_1$



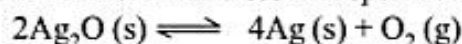
The heat of formation of  $\text{NCl}_3(\text{g})$  in the terms of  $\Delta H_1$ ,  $\Delta H_2$  and  $\Delta H_3$  is

(A)  $\Delta H_f = -\Delta H_1 + \frac{\Delta H_2}{2} - \frac{3}{2}\Delta H_3$  (B)  $\Delta H_f = \Delta H_1 + \frac{\Delta H_2}{2} - \frac{3}{2}\Delta H_3$

(C)  $\Delta H_f = \Delta H_1 - \frac{\Delta H_2}{2} - \frac{3}{2}\Delta H_3$  (D) None

**Ans.** (A)

**Q.13** If  $\text{Ag}_2\text{O}(\text{s})$  is exposed to atmosphere having pressure 1 atm and temperature  $27^\circ\text{C}$ . Under these conditions comment whether it will dissociate spontaneously or not.



Given:	$\Delta H_f^\circ (\text{kJ/mol})$	$\Delta S^\circ (\text{J/Kmol})$ at $27^\circ\text{C}$
$\text{Ag}(\text{s})$	0	42.0
$\text{Ag}_2\text{O}(\text{s})$	-30	121.0
$\text{O}_2(\text{g})$	0	204.0

(Air consist of 20%  $\text{O}_2$  by volume)

Take :  $R = 8.3 \text{ JK}^{-1} \text{ mol}^{-1}$

**Sol.**  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$$\Delta H^\circ = \Delta H_f^\circ (\text{product}) - \Delta H_f^\circ (\text{reactants})$$

$$= 2 \times 30 = 60 \text{ kJ}$$

$$\Delta S^\circ = 204 + 4(42) - 2(121) = +130$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 60000 - 300 \times 130$$

$$\Delta G^\circ = 21000 \text{ J} = -RT \ln K$$

$$\log K = -\left(\frac{21000}{300 \times 8.3 \times 2.3}\right)$$

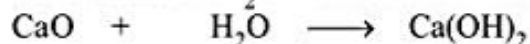
$$K_p = 2.15 \times 10^{-4} \text{ atm}$$

The dissociation of  $\text{Ag}_2\text{O}$  is nonspontaneous at  $27^\circ\text{C}$

- Q.14** A 500 gm sample of water is reacted with an equimolar amount of CaO (both at an initial temp of 25°C). What is the final temperature of the product? [Assume that the product absorbs all of the heat released in the reaction] Heat produced per mol of Ca(OH)<sub>2</sub> is 65.2 kJ and specific heat Ca(OH)<sub>2</sub> is 1.2 J/g°C.  
 (A)  $\approx 735^\circ\text{C}$  (B)  $\approx 760^\circ\text{C}$  (C)  $\approx 746^\circ\text{C}$  (D)  $\approx 789^\circ\text{C}$

**Ans. (B)**

**Sol.** No. of moles of H<sub>2</sub>O = No. of moles of CaO = No. of moles Ca(OH)<sub>2</sub> produced = 500/18



$$\text{Total heat released} = \frac{500}{18} \times 65.2 \times 1000 \text{ J}$$

$$\text{Mass of Ca(OH)}_2 \text{ produced} = \frac{500}{18} \times 74 \text{ gm}$$

$$\therefore \frac{500}{18} \times 74 \times 1.2 \times (T - 25) = \frac{500}{18} \times 65.2 \times 1000$$

$$88.8(T - 25) = 65200 \quad ; \quad T = 734.23 + 25 \Rightarrow 759.23^\circ\text{C}$$

- Q.15** The enthalpy of formation of ethane and benzene from the gaseous atoms are -2839.2 and -5506 KJ/mol respectively. Bond enthalpy of C=C bond is

Given: Resonance energy of benzene = -23.68 KJ/mol

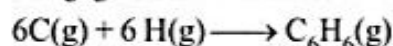
Bond enthalpy of C-H bond = 411.0 KJ/mol

- (A) 373.98 KJ/mol (B) 632.24 KJ/mol (C) 647.5 KJ/mol (D) 1896.72 KJ/mol

**Ans. (B)**

**Sol.**  $-2839.2 = 0 - [6 \times 411 + \Delta H_{\text{C-C}}]$

$$\Delta H_{\text{C-C}} = 373.2 \text{ KJ/mol}$$



$$\Delta H_{\text{theoretical}} = 0 - [6 \times 411 + 3 \times 373.2 + 3x]$$

R.E. = Actual - Theoretical

$$-23.68 = -5506 + [6 \times 411 + 3 \times 373.2 + 3x]$$

$$3x = 5506 - 23.68 - 2466 - 1119.6$$

$$x = 632.24 \text{ KJ/mol} \quad \text{or} \quad \Delta H_{\text{C=C}} = 632.24 \text{ KJ/mol}$$

- Q.16** The reaction  $\text{CH}_4\text{(g)} + \text{Cl}_2\text{(g)} \longrightarrow \text{CH}_3\text{Cl(g)} + \text{HCl(g)}$  has  $\Delta H = -25 \text{ kCal}$ .

Bond	Bond Energy kCal
$\epsilon_{\text{C-Cl}}$	84
$\epsilon_{\text{H-Cl}}$	103
$\epsilon_{\text{C-H}}$	x
$\epsilon_{\text{Cl-Cl}}$	y
x : y = 9 : 5	

From the given data, what is the bond energy of Cl—Cl bond

- (A) 70 kCal (B) 80 kCal (C) 67.75 kCal (D) 57.75 kCal

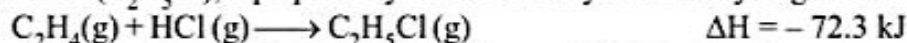


Ans. (D)

Sol.  $-25 \times 10^3 \text{ cal} = +E_{\text{C-H}} + E_{\text{Cl-Cl}} - (E_{\text{C-Cl}} + E_{\text{H-Cl}}) = x + y - (84 \times 10^3 + 103 \times 10^3) \text{ cal}$   
 $x + y = 162 \times 10^3 \text{ cal}$

$$\frac{9}{5}y + y \quad ; \quad y = \frac{162 \times 10^3}{\left(1 + \frac{9}{5}\right)} \text{ cal} = 57.75 \text{ Kcal}$$

Q.17 Ethyl chloride ( $\text{C}_2\text{H}_5\text{Cl}$ ), is prepared by reaction of ethylene with hydrogen chloride:



What is the value of  $\Delta E$  (in kJ), if 98 g of ethylene and 109.5 g of HCl are allowed to react at 300 K.

(A) -64.81 (B) -190.71 (C) -209.41 (D) -224.38

Ans. (C)

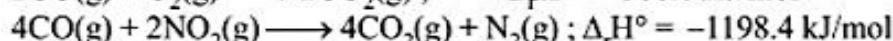
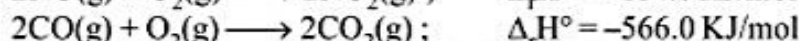
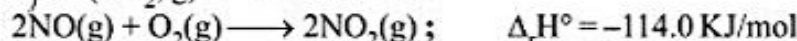
Sol. No. of mole of  $\text{C}_2\text{H}_4 = \frac{98}{28} = 3.5$ , No. of mole of HCl (Limiting Reagent) =  $\frac{109.5}{36.5} = 3$

$$\Delta H = \Delta E + \Delta n_g RT \quad ; \quad -72.3 = \Delta E + (-1 \times 8.314 \times 300)/1000$$

$$\Delta E = -69.80 \text{ ; for three mole } \Delta E = -69.80 \times 3 \Rightarrow -209.41 \text{ kJ/mol} \quad \text{Ans.}$$

Q.18 (i) Determine  $\Delta_f H^\circ$  ( $\text{NO}$ , g) at  $25^\circ\text{C}$ . Using the following information

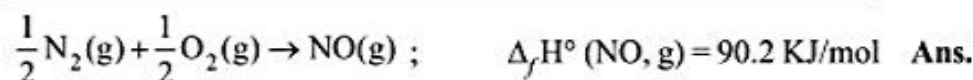
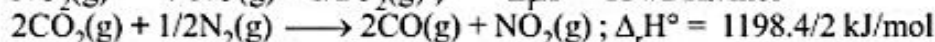
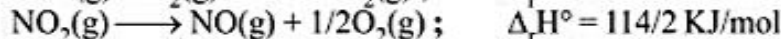
$$\Delta_f H^\circ (\text{CO}_2, \text{g}) = -393.5 \text{ KJ/mol}$$



(ii) Calculate the equilibrium pressure (in Pascal) for the conversion of graphite to diamond at  $25^\circ\text{C}$ . The densities of graphite and diamond may be taken to be 2.20 and 3.40 g/cc respectively independent of pressure.

$$\text{Given : } \Delta G^\circ (\text{C (graphite)} \rightarrow \text{C (diamond)}) = 2900 \text{ J/mol.}$$

Sol. (i)  $2\text{CO}(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{CO}_2(\text{g}) \quad ; \quad \Delta_r H^\circ = -566.0 \text{ KJ/mol}$



(ii)  $\Delta G_2 - \Delta G_1 = \Delta V[P_2 - P_1]$

$$\Delta V = 12 \times \left[ \frac{1}{3.4} - \frac{1}{2.2} \right] \times 10^{-6} \text{ m}^3 \text{mol}^{-1}$$

$$\Delta V = -\frac{14.4}{3.4 \times 2.2} \times 10^{-6} \Rightarrow -1.925 \times 10^{-6} \text{ m}^3 \text{mol}^{-1}$$

Let  $P_2$  is equilibrium pressure;  $\Delta G_2 = 0$ ;  $P_2 = 1 \text{ bar} = 10^5 \text{ Pa}$

$$0 - \Delta G_1 = -1.925 \times 10^{-6} [P_2 - 1]$$

$$2900 = 1.925 \times 10^{-6} [P_2 - P_1]$$

$$P_2 = \frac{2900}{1.925 \times 10^{-6}} + P_1$$

$$\Rightarrow 1506.5 \times 10^6 + 10^5$$

$$P_2 = 1.50 \times 10^9 \text{ Pa} \quad \text{Ans.}$$



**Q.19** Which of the following do(es) not represent  $\Delta H$  formation of the product.

- (I)  $\frac{1}{2} \text{H}_2(\text{g}) + (\text{aq}) \longrightarrow \text{H}^+(\text{aq})$       (II)  $\frac{2}{3} \text{O}_3(\text{g}) \longrightarrow \text{O}_2(\text{g})$   
 (III)  $\text{NH}_4^+(\text{g}) + \text{Cl}^-(\text{g}) \longrightarrow \text{NH}_4\text{Cl}(\text{s})$       (IV)  $\text{P}_4(\text{black}) + 5\text{O}_2(\text{g}) \longrightarrow \text{P}_4\text{O}_{10}(\text{s})$   
 (V) Reaction representing  $\Delta H_{\text{combustion}}$  of C (graphite).  
 (A) I, IV, V      (B) II, IV      (C) II, III, IV      (D) II, III, IV, V

**Ans.** (C)

**Sol.** (I)  $\Delta H_f$  of  $\text{H}^+$

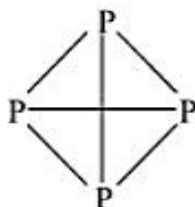
(V)  $\Delta H_f$  of  $\text{CO}_2(\text{g})$

$\therefore \text{II} \rightarrow \text{O}_2(\text{g}) \longrightarrow \text{O}_2(\text{g}) \quad \Delta H_f \text{O}_2$

$\text{III} \rightarrow \frac{1}{2} \text{N}_2 + 2\text{H}_2 + \frac{1}{2} \text{Cl}_2 \quad \Delta H_f \text{NH}_4\text{Cl}$

$\text{IV} \rightarrow \text{P}_4(\text{white}) + \dots \quad \Delta H_f \text{P}_4\text{O}_{10} \quad ; \text{option (C)}$

**Q.20** White phosphorus is a tetra-atomic solid  $\text{P}_4(\text{s})$  at room temperature.



Find average (P-P) bond enthalpy in kJ/mol.

Given:  $\Delta H_{\text{sublimation}}$  of  $\text{P}_4(\text{s}) = 59 \text{ kJ/mol}$

$\Delta H_{\text{atomisation}}$  of  $\text{P}_4(\text{s}) = 1265 \text{ kJ/mol}$

**Sol.**  $(\text{P-P}) = \frac{1265 - 59}{6} = 201$

**Q.21** Calculate the strength of H-bond between  $\text{F}^-(\text{g})$  and  $\text{CH}_3\text{COOH}(\text{g})$  from the given data.

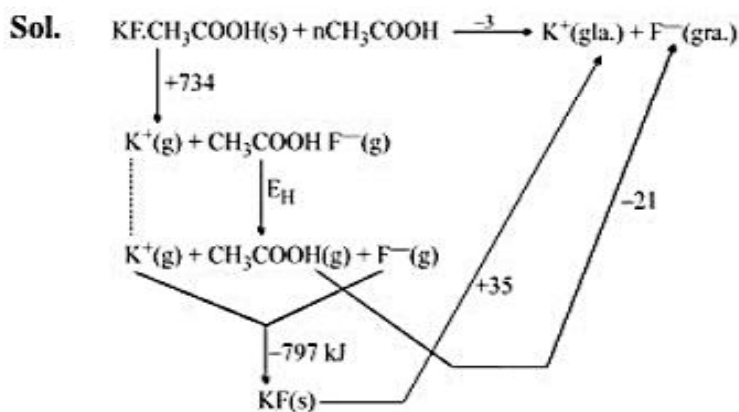
$\Delta H_{\text{solution}} [\text{KF} \cdot \text{CH}_3\text{COOH}(\text{s})]$  in glacial acetic acid =  $-3 \text{ kJ/mole}$

$\Delta H_{\text{solution}} [\text{KF}(\text{s})]$  in glacial acetic acid =  $+35 \text{ kJ/mole}$

Lattice Enthalpy  $\text{KF}(\text{s})$  =  $+797 \text{ kJ/mole}$

Lattice enthalpy of  $\text{KF} \cdot \text{CH}_3\text{COOH}(\text{s})$  =  $+734 \text{ kJ/mole}$

$\Delta H_{\text{vaporization}} [\text{CH}_3\text{COOH}(\text{l})]$  =  $+21 \text{ kJ/mole}$



$$-3 = +734 + E_H - 797 + 35 - 21$$

$$E_H = -3 - 734 - 35 + 797 + 21 = +46 \text{ kJ/mole}$$

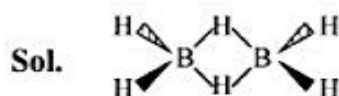
**Q.22** Find the Bond enthalpy (in kJ/mol) of one "three centre two electron bond" in  $B_2H_6$  {B-H-B  $\rightarrow$  2B(g) + H(g)} from the given data.

$$\Delta H_f^\circ [BH_3(g)] = 100 \text{ kJ/mole}$$

$$\Delta H_f^\circ [B_2H_6(g)] = 36 \text{ kJ/mole}$$

$$\Delta H_{\text{atm}} [B(s)] = 565 \text{ kJ/mole}$$

$$\Delta H_{\text{atm}} [H_2(g)] = 218 \text{ kJ/mole}$$



B. E. of B-H:

$$3E_{B-H} = 565 + 654 - 100$$

$$E_{B-H} = 373$$

$$B(s) + \frac{3}{2} H_2 \xrightarrow{100} BH_3(g)$$

$$\begin{array}{ccc} \downarrow +565 & \downarrow 3 \times 218 & \downarrow 3E_{B-H} \\ B(g) + 3H(g) & & \end{array}$$

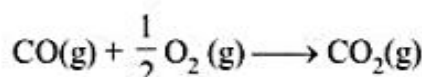
$$2B(s) + 3H_2(g) \xrightarrow{+36} B_2H_6$$

$$\begin{array}{ccc} \downarrow & & \downarrow \\ 2B(g) + 6H(g) & \xleftarrow{4E_{B-H} + 2E_{B-H-B}} & \end{array}$$

$$2E_{B-H-B} = 2 \times 565 + 6 \times 218 - 36 - 4 \times 373$$

$$E_{B-H-B} = 455 \text{ kJ/mol} = 4.55 \times 10^2 \text{ kJ/mole}$$

**Q.23** For the reaction



using data given in table find out incorrect statement(s) among the following.

	$\Delta H_f^\circ$ (kJ / mole)	$S^\circ$ (J / K mole)
CO(g)	-110	+197
O <sub>2</sub> (g)	0	+205
CO <sub>2</sub> (g)	-395	+213

Assume vibration modes of motion do not contribute to heat capacity at low temperature.

(A)  $\Delta H^\circ > \Delta U^\circ$  for the reaction at 298K.

(B) In standard state condition, the reaction  $CO(g) + \frac{1}{2} O_2(g) \longrightarrow CO_2(g)$  attain equilibrium at very high temperature.

(C) At low temperature  $\frac{d(\Delta H)^\circ}{dT} = -ve$

(D) In a CO, O<sub>2</sub> fuel cell electrical energy obtained by cell  $> |\Delta H_{\text{combustion}}^\circ [CO(g)]|$

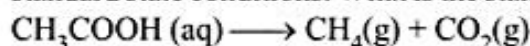
**Ans.** (A)

**Sol.**  $\Delta H^\circ - \Delta U^\circ = \Delta n_g RT$   
 since  $\Delta n_g = -ve$   
 $\Rightarrow \Delta H^\circ - \Delta U^\circ \leq 0$

$$\Delta H^\circ = -ve$$

$$\Delta S^\circ = -ve \quad ; \quad C_p = \frac{3}{2}R + R \quad ; \quad = \frac{5}{2}R \quad ; \quad \Delta_r C_p = -ve$$

**Q.24** At temperatures above 85 K, decarboxylation of acetic acid becomes a spontaneous process under standard state conditions. What is the standard entropy change (in J/K-mol) of the reaction.



$$\text{Given: } \Delta_f H^\circ [\text{CH}_3\text{COOH (aq)}] = -484 \text{ kJ/mole}$$

$$\Delta_f H^\circ [\text{CO}_2\text{(g)}] = -392 \text{ kJ/mole}$$

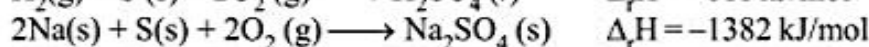
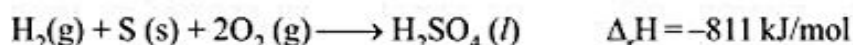
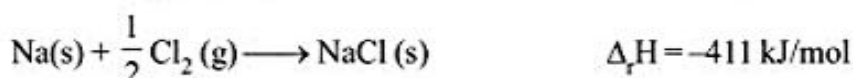
$$\Delta_f H^\circ [\text{CH}_4\text{(g)}] = -75 \text{ kJ/mole}$$

**Sol.** At 85 K the process must be at equilibrium under standard state condition:

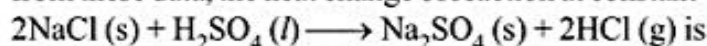
$$\Delta G^\circ = 0$$

$$\Delta H^\circ = T\Delta S^\circ \Rightarrow \Delta S^\circ = \frac{\Delta H^\circ}{T} = \frac{[-392 - 75 - (-484)] \times 10^3}{85} = 2.00 \times 10^2 \text{ J/K-mol}$$

**Q.25** The enthalpy changes of the following reactions at 27°C are

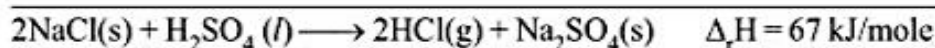
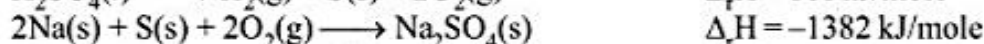
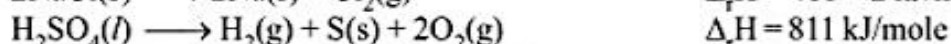


from these data, the heat change of reaction at constant volume (in kJ/mol) at 27°C for the process



(A) 67 (B) 62.02 (C) 71.98 (D) None

**Ans. (B)**



$$67 = \Delta_r U + \frac{2 \times 8.3 \times 300}{1000}; \quad \Delta_r U = 62.02 \text{ kJ/mole}$$

**Q.26** Calculate  $|\Delta_f G^\circ|$  for  $(\text{NH}_4\text{Cl, s})$  at 350 K.

$$\text{Given: } \Delta_f H^\circ (\text{NH}_4\text{Cl, s}) = -314.5 \text{ kJ/mol}$$

$$S^\circ_{\text{N}_2\text{(g)}} = 192 \text{ JK}^{-1}\text{mol}^{-1}; \quad S^\circ_{\text{H}_2\text{(g)}} = 130.5 \text{ JK}^{-1}\text{mol}^{-1}$$

$$S^\circ_{\text{Cl}_2\text{(g)}} = 223 \text{ JK}^{-1}\text{mol}^{-1}; \quad S^\circ_{\text{NH}_4\text{Cl(s)}} = 94.5 \text{ JK}^{-1}\text{mol}^{-1}; \quad \text{All given data at 300K.}$$

$$\Delta_r C_p = -20 \text{ J/mol-K}; \quad \ln\left(\frac{350}{300}\right) = 0.15$$

**Sol.**  $\Delta_f S^\circ (\text{NH}_4\text{Cl}, s) \text{ at } 300 \text{ K} = S^\circ_{\text{NH}_4\text{Cl}(s)} - \left[ \frac{1}{2} S^\circ_{\text{N}_2} + 2S^\circ_{\text{H}_2} + \frac{1}{2} S^\circ_{\text{Cl}_2} \right]$

$$= 94.5 - \left( \frac{1}{2} \times 192 + 2 \times 130.5 + \frac{1}{2} \times 223 \right)$$

$$= 94.5 - (96 + 261 + 111.5)$$

$$\Delta_f S^\circ_{300} = -374 \text{ JK}^{-1}\text{mol}^{-1}$$

$$\Delta_f S^\circ_{310} = \Delta_f S^\circ_{300} + \Delta_r C_p \ln \left( \frac{350}{300} \right)$$

$$= -374 - 20 \times (0.15) = -377 \text{ JK}^{-1}\text{mol}^{-1}$$

$$\Delta_f H^\circ_{310} = \Delta_f H^\circ_{300} + \Delta_r C_p [350 - 300]$$

$$= -314.5 - \frac{20 \times 50}{1000} = -315.5$$

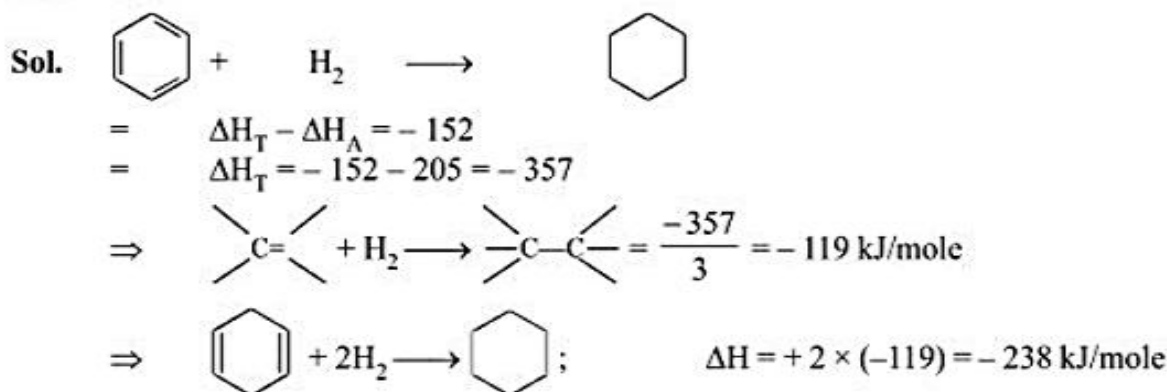
$$\Delta_f G^\circ_{350} = \Delta_f H^\circ - T \Delta_f S^\circ$$

$$= -315.5 - \frac{350 \times (-377)}{1000} \Rightarrow -183.55 \text{ kJ/mol}$$

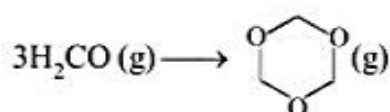
$$|\Delta_f G^\circ_{350}| = 183.55 \text{ kJ/mol} \Rightarrow 183 \text{ kJ/mol}$$

- Q.27** If enthalpy of hydrogenation of  $\text{C}_6\text{H}_6(l)$  into  $\text{C}_6\text{H}_{12}(l)$  is  $-205 \text{ kJ}$  & resonance energy of  $\text{C}_6\text{H}_6(l)$   $-152 \text{ kJ/mol}$  then enthalpy of hydrogenation of 1,4-cyclohexadiene ( $l$ ) is  
 Assume  $\Delta H_{\text{vap}}$  of  $\text{C}_6\text{H}_6(l)$ ,  $\text{C}_6\text{H}_8(l)$ ,  $\text{C}_6\text{H}_{12}(l)$  all are equal  
 (A)  $-535.5 \text{ kJ/mol}$  (B)  $-238 \text{ kJ/mol}$  (C)  $-357 \text{ kJ/mol}$  (D) None

**Ans. (B)**



- Q.28** The enthalpy of gas phase trimerization of one mole of gaseous formaldehyde in (kJ/mole)



Bond energies (kJ/mole)

$\epsilon_{\text{C=O}}$	$\epsilon_{\text{C-O}}$	$\epsilon_{\text{C-H}}$
700	360	410

(A)  $-20$

(B)  $-60$

(C)  $-10$

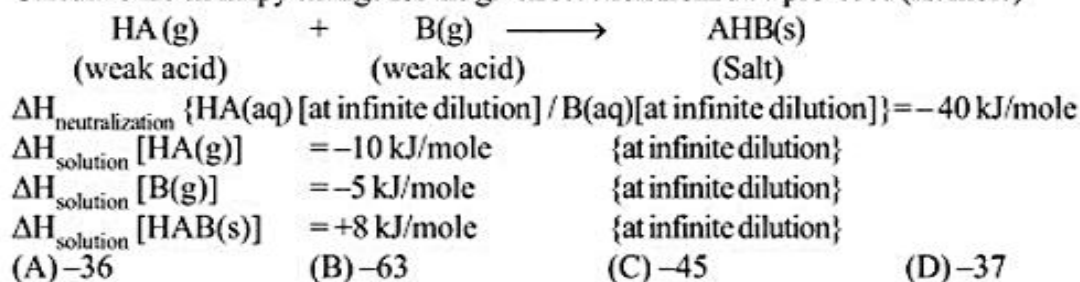
(D)  $-50$

**Ans. (A)**

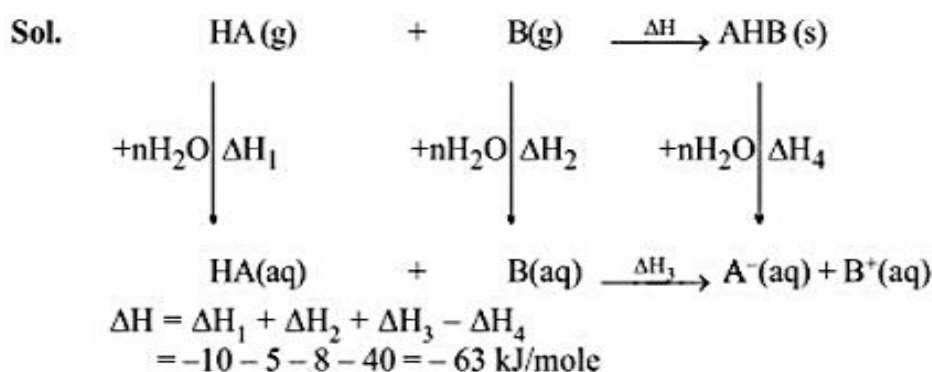


Sol.  $\Delta H = \epsilon_{C=O} - 2 \epsilon_{C-O} \Rightarrow 700 - 720 = -20 \text{ kJ/mole}$




Q.29 Calculate the enthalpy change for the given reaction from data provided (kJ/mole)

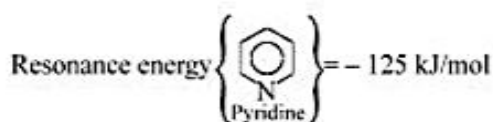


Ans. (B)




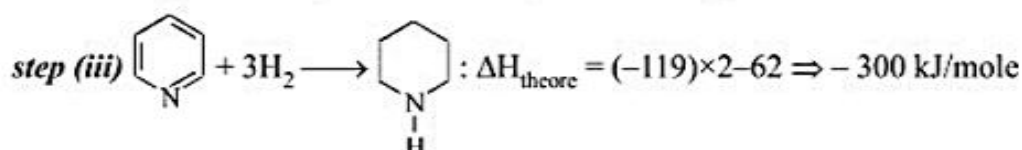
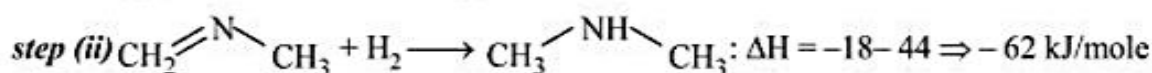
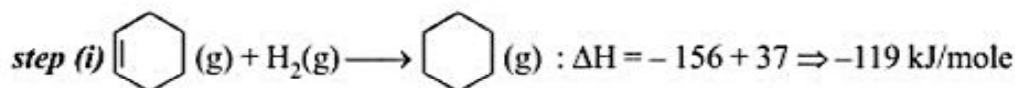
Q.30 Estimate  $\Delta H_f^\circ$  {pyridine (l)} from the given data.

Compound	$\Delta H_{f,298 \text{ K}}^\circ$ in kJ/mole
$\text{CH}_2=\text{N}-\text{CH}_3(\text{g})$	+ 44
$\text{CH}_3-\text{NH}-\text{CH}_3(\text{g})$	- 18
 (g)	- 37
 (g)	- 156
 N-H(g)	- 50



Sol.

$\Delta H$  of Hydrogenation of 



$\Delta H_{\text{actual}} \text{ for (iii)} = -300 + \frac{125}{\text{R.E.}} = \boxed{-175 \text{ kJ/mole}}$       Ans.

$$\Delta H_f \left\{ \text{C}_6\text{H}_5\text{NH}_2(\text{g}) \right\} - \Delta H_f \left\{ \text{C}_6\text{H}_5\text{N}(\text{g}) \right\} \Rightarrow -175$$

$$\Delta H_f^\circ \left\{ \text{C}_6\text{H}_5\text{N}(\text{g}) \right\} = -50 + 175 \Rightarrow +125$$

*final step*  $\Delta H_f^\circ \left\{ \text{C}_6\text{H}_5\text{N}(\text{g}) \right\} = +125 - 40 \Rightarrow \boxed{+85 \text{ kJ / mole}}$       Ans.

- Q.31** The standard enthalpy of atomisation of  $\text{PCl}_3(\text{g})$  is 195 Kcal/mol. What will be the standard enthalpy of atomisation of  $\text{PCl}_5(\text{g})$ , if the bond dissociation energies of axial P–Cl bonds in  $\text{PCl}_5(\text{g})$  are 10% lesser and the bond dissociation energies of equatorial P–Cl bonds in  $\text{PCl}_5(\text{g})$  are 10% higher than the bond dissociation energies of P–Cl bonds in  $\text{PCl}_3(\text{g})$ .

(A) 195 Kcal / mol      (B) 325 Kcal / mol      (C) 331.5 Kcal / mol      (D) 318.5 Kcal / mol

**Ans.** (C)



$$3\text{BE}_{\text{P-Cl}} = 195 \text{ kcal/mol}$$

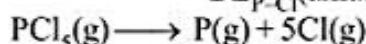
$$\text{BE}_{\text{P-Cl}} = 65 \text{ kcal/mole}$$

equatorial

in  $\text{PCl}_5$       3P–Cl bonds are equatorial

$$\text{BE}_{\text{P-Cl}}(\text{eq}) = 65 \times 1.1 = 71.5 \text{ kcal}$$

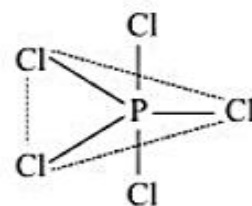
$$\text{BE}_{\text{P-Cl}}(\text{axial}) = 65 \times 0.9 = 58.5 \text{ kcal}$$



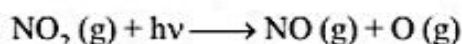
$$3\text{BE}_{\text{P-Cl}} + 3\text{BE}_{\text{P-Cl}}(\text{axial}) = 3 \times 71.5 + 2 \times 58.5 = 331.5 \text{ kcal}$$

(equatorial)

$$\Delta H = 331.5 \text{ kcal.}$$



- Q.32** An important reaction in production of smog is

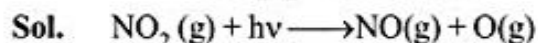


If light of wavelength  $4.4 \times 10^{-7} \text{ m}$  is used to cause above reaction. Calculate N–N bond enthalpy.

Given:  $\Delta H_f[\text{NO}(\text{g})] = 91 \text{ kJ mol}^{-1}$  ;       $h = 6.6 \times 10^{-34} \text{ J s}$

$\Delta H_f[\text{N}_2\text{O}_4(\text{g})] = 9 \text{ kJ mol}^{-1}$  ;       $c = 3 \times 10^8 \text{ ms}^{-1}$

$\Delta H_{\text{O=O}} = 498 \text{ kJ mol}^{-1}$  ;       $N_A = 6 \times 10^{23}$



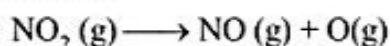
$\Delta H$  for the reaction

$$\Delta H = N_A \times \frac{hc}{\lambda}$$

$$= 6 \times 10^{23} \times \frac{6.6 \times 10^{-34} \times 3 \times 10^8}{4.4 \times 10^{-7}}$$

$$= +270 \text{ kJ mol}^{-1}$$

for the reaction,



$$\Delta_r H = \sum \Delta H_f \text{ Product} - \sum \Delta H_f \text{ Reactant}$$

$$+ 270 \text{ kJ mol}^{-1} = 91 + \frac{498}{2} - \Delta H_f \text{ NO}_2(\text{g})$$

$$\Delta H_f(\text{NO}_2)(\text{g}) = + 70 \text{ kJ mol}^{-1}$$

Now for the reaction,



$$\Delta_r H = \sum \Delta H_f \text{ Product} - \sum \Delta H_f \text{ Reactant}$$

$$= + 9 - (2 \times 70) = - 131 \text{ kJ mol}^{-1}$$

Thus bond energy for N–N bond = + 131 kJ mol<sup>-1</sup>

## CHEMICAL KINETICS

Chemical kinetics is the branch of physical chemistry that deals with the study of rate of reactions and the factors governing rate of reaction.

Important applications of kinetic studies are given below :

1. In determination of rates of reactions and factors governing rates.
2. In predicting the conditions for maintaining the reaction rate
3. In determination of yield of reaction in certain time period.
4. In calculating the time required for completion of a reaction.
5. In deciding the mechanism of a reaction.

### 1. TYPES OF REACTIONS

On the basis of reaction rates, the chemical reactions have been classified into the following three groups:-

- (i) **Very fast or instantaneous reactions :** These reactions occur at a very fast rate. Generally these reactions involve ionic species and known as ionic reactions.

These reactions take about  $10^{-14}$  seconds for completion.

Examples: (i)  $\text{AgNO}_3 + \text{NaCl} \rightarrow \text{AgCl} + \text{NaNO}_3$  (Precipitation reaction)  
(Ppt.)

(ii)  $\text{HCl} + \text{NaOH} \rightarrow \text{NaCl} + \text{H}_2\text{O}$  (Neutralization reaction)  
(acid) (base) (salt)

- (ii) **Moderate reaction :** These type of reactions proceed with a measurable rates at normal temperature. In this a large number of bonds have to be broken in reactants molecules and a large number of new bonds have to be formed in product molecules. Mostly these reactions are molecular in nature.

Examples :

(i) Decomposition of  $\text{H}_2\text{O}_2$  :  $2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$

(ii) Decomposition of  $\text{N}_2\text{O}_5$  :  $2\text{N}_2\text{O}_5 \rightarrow 2\text{N}_2\text{O}_4 + \text{O}_2$

(iii) Hydrolysis of ester :  $\text{CH}_3\text{COOC}_2\text{H}_5 + \text{NaOH} \rightarrow \text{CH}_3\text{COONa} + \text{C}_2\text{H}_5\text{OH}$

(iv) Reaction of NO with chlorine :  $\text{NO} + \text{Cl}_2 \rightarrow \text{NOCl}_2$

(v) Inversion of cane sugar in aqueous solution :  $\text{C}_{12}\text{H}_{22}\text{O}_{11} + \text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + \text{C}_6\text{H}_{12}\text{O}_6$   
Glucose Fructose

(vi)  $2\text{FeCl}_3(\text{aq.}) + \text{SnCl}_2 \rightarrow 2\text{FeCl}_2(\text{aq.}) + \text{SnCl}_4(\text{aq.})$

(vii)  $\text{NO}_2 + \text{CO} \rightarrow \text{NO} + \text{CO}_2$

(viii) Decolourisation of acidified potassium permanganate with sodium oxalate.

- (iii) **Very slow reactions :** These reactions are extremely slow and take months together to show any measurable change. The rate of such type of reactions are very slow. So, it is also very difficult to determine the rate of these reactions.

Examples :

(i) Rusting of iron :  $\text{Fe}_2\text{O}_3 + x\text{H}_2\text{O} \rightarrow \text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$   
Hydrated ferric oxide (Rust)

(ii) Reaction between  $\text{H}_2$  and  $\text{O}_2$  to form  $\text{H}_2\text{O}$  at ordinary temperature in absence of catalyst.

(iii) Reaction of atmospheric  $\text{H}_2\text{S}$  on basic lead acetate paint.

White basic lead acetate paint  $\xrightarrow[\text{H}_2\text{S}]{\text{atmospheric}}$  Blackening of paint very slowly  
(due to formation of PbS)



**Note :** The chemical reactions can be slowed down or speed up by changing conditions under which they occur. e.g.  $\text{CO} + 2\text{H}_2 \xrightarrow[\text{temp.}]{\text{At room}} \text{CH}_3\text{OH}$  (very slow reaction)

The reaction can be speeded up by maintaining temperature around  $400^\circ\text{C}$ , pressure about 300 atm and using a catalyst containing  $\text{ZnO}$  and  $\text{Cr}_2\text{O}_3$ .

## 2. RATE OF REACTION

The change in concentration of either reactant or product per unit time.

Formula :  $r = \frac{dc}{dt}$

dc is change in concentration of reactant or product in a small time interval dt.



(i) Rate of formation of ammonia  $= + \frac{d[\text{NH}_3]}{dt}$

(ii) Rate of disappearance of nitrogen  $= - \frac{d[\text{N}_2]}{dt}$

(iii) Rate of disappearance of hydrogen  $= - \frac{d[\text{H}_2]}{dt}$

$$\text{Rate of reaction} = + \frac{1}{2} \frac{d[\text{NH}_3]}{dt} = - \frac{d[\text{N}_2]}{dt} = - \frac{1}{3} \frac{d[\text{H}_2]}{dt}$$

### 2.1 AVERAGE RATE AND INSTANTANEOUS RATE OF REACTION

A difficulty arises in stating the rate of reaction as above. This is because according to the Law of Mass Action, the rate of reaction depends upon the molar concentrations of reactants which keep on decreasing with the time (while those of the products keep on increasing). Therefore, the rate of reaction does not remain constant throughout.

Thus the rate of reaction as defined above is the 'average rate of reaction' during the time interval chosen.

To know the rate of reaction at any instant of time during the course of a reaction, we introduce the term 'instantaneous rate of reaction' which may be defined as follows :

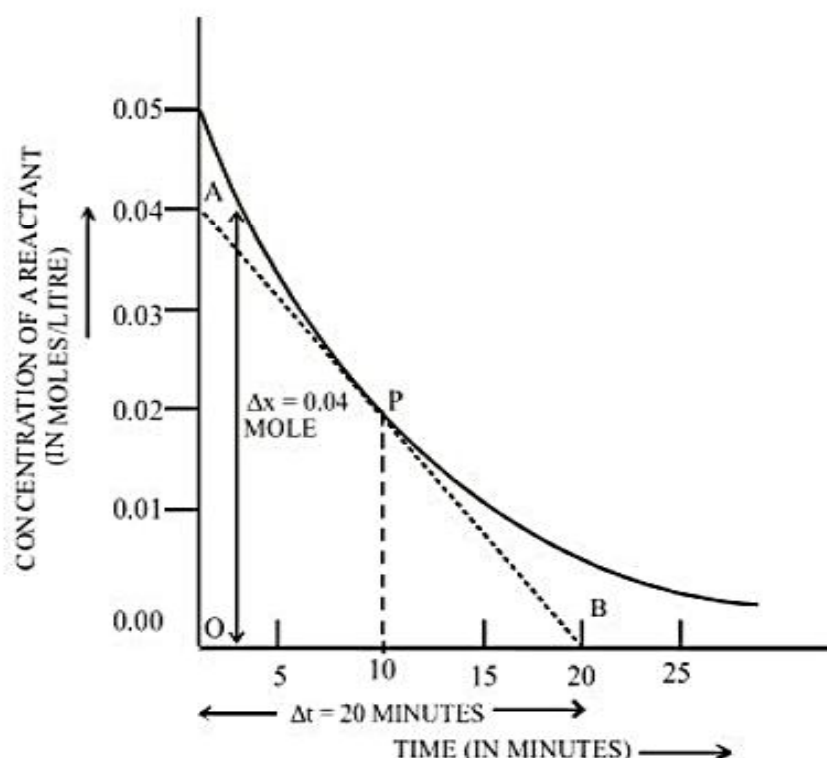
The rate of reaction at any instant of time is the rate of change of concentration (i.e. change of concentration per unit time) of any one of the reactants or products at that particular instant of time.

To express the instantaneous rate of reaction, as small interval of time (dt) is chosen at that particular instant of time during which the rate of reaction is supposed to be almost constant. Suppose the small change in concentration is dx in the small interval of time dt. Then the rate of reaction at that

instant is given by  $\frac{dx}{dt}$ .

## 2.2 Measurement of the Rate of Reaction

In order to measure the rate of a reaction, the progress of the reaction is followed by studying the concentration of one of the reactants or products at different intervals of time. The most common practice to do so is to withdraw small amount of the reaction mixture ( $2\text{ cm}^3$  or  $5\text{ cm}^3$ ) at different intervals of time, cool it down immediately to nearly  $0^\circ\text{C}$  to arrest the reaction (called freezing the reaction) and then find out the concentration of the reactant or the product by suitable method usually by titration against a suitable reagent. However, this method is not preferred when some observable property like volume, pressure, optical rotation etc. changes with time and can be observed directly at different intervals of time without stopping the reaction. It is important to mention that except concentration, all other factors (like temperature etc.) which affect the rate of the reaction are kept constant during the kinetic study of the reaction.



If concentration of one of the reactants is studied at different intervals of time and these values are plotted against the corresponding times, a graph of the type shown in figure may be obtained.

## 2.3 Calculation of instantaneous rate of reaction

To know the rate of the reaction at any time  $t$ , a tangent is drawn to the curve at the point corresponding to that time figure and it is extended on either side so as to cut the axes, say at the points A and B. Then

$$\begin{aligned}\text{Rate of reaction} &= \frac{\text{Change in the concentration}}{\text{Time}} \\ &= \frac{\Delta x}{\Delta t} = \frac{OA}{OB} \text{ Slope of the tangent}\end{aligned}$$

Thus the slope of the tangent gives the rate of reaction.

For example, from the (figure) in the present case, at time  $t = 10$  minutes,  $\Delta x = 0.04$  mole and  $\Delta t = 20$  minutes  $= 20 \times 60 = 1200$  seconds, therefore, rate of reaction at the end of 10 minutes will be  $0.04/1200 = 3.33 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}$ .

## 2.4 Calculation of the average rate of reaction :

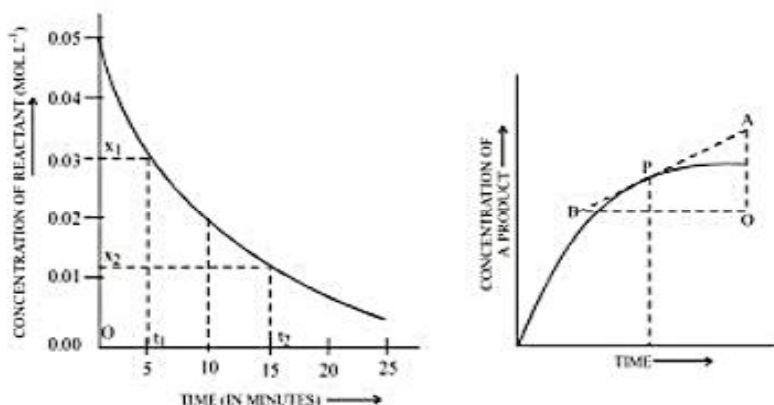
To calculate the average rate of reaction between any two instants of time say  $t_1$  and  $t_2$ , the corresponding concentrations  $x_1$  and  $x_2$  are noted from the graph. Then

$$\text{Average rate of reaction} = \frac{x_2 - x_1}{t_2 - t_1}$$

For example, from the (figure) between the time interval 5 to 15 minutes,

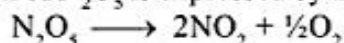
$$\text{Average rate} = \frac{0.03 - 0.012}{15 - 5} = \frac{0.018}{10} = 0.0018 \text{ and mol L}^{-1} \text{ min}^{-1}$$

If concentration of one of the products is plotted against time, the type of curve obtained and the rate of reaction at any instant of time are calculated as shown in the figure.



### Illustration

1. Decomposition of  $\text{N}_2\text{O}_5$  is expressed by the equation,



If in a certain time interval, rate of decomposition of  $\text{N}_2\text{O}_5$  is  $1.8 \times 10^{-3} \text{ mol litre}^{-1} \text{ min}^{-1}$ , what will be the rates of formation of  $\text{NO}_2$  and  $\text{O}_2$  during the same interval?

**Sol.** The rate expression for the decomposition of  $\text{N}_2\text{O}_5$  is

$$-\frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t} = \frac{1}{2} \frac{\Delta[\text{NO}_2]}{\Delta t} = 2 \times \frac{\Delta[\text{O}_2]}{\Delta t}$$

$$\begin{aligned} \text{So } \frac{\Delta[\text{NO}_2]}{\Delta t} &= 2 \frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t} = 2 \times 1.8 \times 10^{-3} \\ &= 3.6 \times 10^{-3} \text{ mol litre}^{-1} \text{ min}^{-1} \end{aligned}$$

$$\begin{aligned} \text{and } \frac{\Delta[\text{O}_2]}{\Delta t} &= \frac{1}{2} \frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t} = \frac{1}{2} \times 1.8 \times 10^{-3} \\ &= 0.9 \times 10^{-3} \text{ mol litre}^{-1} \text{ min}^{-1} \end{aligned}$$

[Magnitude of rate is always positive and hence  $= \frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t}$  is taken positive.]

2. A gaseous reaction :  $2\text{A}(\text{g}) + \text{B}(\text{g}) \rightarrow 2\text{C}(\text{g})$ ,

Show a decrease in pressure from 120 mm to 100 mm in 10 minutes. The rate of appearance of C is

- (A) 2 mm/min      (B) 4 mm/min      (C) 10 mm/min      (D) 12 mm/min.



**Ans. (B)**

**Sol.** Suppose  $2p$  is the pressure of C after 10 min.

Fall in pressure of A =  $2p$  ; Fall in pressure of B =  $p$

Total fall in pressure =  $(2p + p) - 2p = p = 20$  mm

Pressure of C =  $2p = 40$  mm

Rate of appearance of C =  $40/10 = 4$  mm/min

**3.** For the reaction :  $4\text{NH}_3(\text{g}) + 5\text{O}_2(\text{g}) \rightarrow 4\text{NO}(\text{g}) + 6\text{H}_2\text{O}(\text{g})$

Given :  $\frac{d[\text{NO}]}{dt} = 3.6 \times 10^{-3} \text{ mol l}^{-1} \text{ s}^{-1}$

Calculate : (i) rate of disappearance of ammonia (ii) rate of formation of water

**Sol.** From the eqn. it is clear that

$$\text{Rate} = -\frac{1}{4} \frac{d[\text{NH}_3]}{dt} = \frac{1}{4} \frac{d[\text{NO}]}{dt} = \frac{1}{6} \frac{d[\text{H}_2\text{O}]}{dt} \quad \text{Thus : } -\frac{1}{4} \frac{d[\text{NH}_3]}{dt} = \frac{1}{4} \frac{d[\text{NO}_2]}{dt}$$

$$\text{or } -\frac{d[\text{NH}_3]}{dt} = \frac{d[\text{NO}_2]}{dt} = 3.6 \times 10^{-3} \text{ mol l}^{-1} \text{ s}^{-1} \quad \text{Also } \frac{1}{4} \cdot \frac{d[\text{NO}]}{dt} = \frac{1}{6} \cdot \frac{d[\text{H}_2\text{O}]}{dt}$$

$$\frac{3}{2} \cdot \frac{d[\text{NO}]}{dt} = \frac{d[\text{H}_2\text{O}]}{dt}$$

$$\frac{3}{2} \times 3.6 \times 10^{-3} = \frac{d[\text{H}_2\text{O}]}{dt}$$

$$5.4 \times 10^{-3} = \frac{d[\text{H}_2\text{O}]}{dt}$$

### Exercise

In a reaction the concentration of a reactant (A) changes from  $0.200 \text{ mol litre}^{-1}$  to  $0.150 \text{ mol litre}^{-1}$  in 10 minutes. What is the average rate of reaction during this interval?

**Ans.**  $0.005 \text{ mol litre}^{-1} \text{ min}^{-1}$

## 2.5 Factors Affecting the Rate of Reaction

- (i) **Concentration** : According to law of mass action greater is the conc. of the reactants, the more rapidly the reaction proceeds.
- (ii) **Pressure (Gaseous reaction)** : On increasing the pressure, volume decreases and conc. increases and hence the rate increases.
- (iii) **Temperature** : It is generally observed that rise in temperature increases the reaction rate. It has been found that rate is either doubled or tripled for every  $10^\circ\text{C}$  rise in temperature.



- (iv) **Nature of the reactants :** The rate depends upon specific bonds involved and hence on the nature of reactants.
- (v) **Surface area of the reactants :** In heterogeneous reactions, more powered is the form of reactants, more is the rate. [as more active centres are provided]
- (vi) **Catalyst :** Affects the rate immensely.

### 3. LAW OF MASS ACTION, RATE LAW AND RATE CONSTANT

- 3.1 Law of mass action :** (Guldberg and Wage 1864) This law relates rate of reaction with active mass or molar concentration of reactants. According to this law, "At a given temperature, the rate of a reaction at a particular instant is proportional to the product of the reactants at that instant raised to powers which are numerically equal to the numbers of their respective molecules in the stoichiometric equation describing the reactions."

Active mass = Molar concentration of the substance

$$= \frac{\text{Number of gram mole of the substance}}{\text{Volume in litres}} = \frac{W/M}{V} = \frac{n}{V}$$

Where W = mass of the substance, M is the molecular mass in grams, 'n' is the number of g moles and V is volume in litre.

Consider the following general reaction,  $m_1A_1 + m_2A_2 + m_3A_3 \rightarrow \text{Products}$

$$\text{Rate of reaction} \propto [A_1]^{m_1} [A_2]^{m_2} [A_3]^{m_3}$$

- 3.2 Rate law :** The actual relationship between the concentration of reacting species and the reaction rate is determined experimentally and is given by the expression called rate law.

For any hypothetical reaction,  $aA + bB \rightarrow cC + dD$

Rate law expression may be,  $\text{rate} = k[A]^m[B]^n$

Where m and n are constant numbers or the powers of the concentrations of the reactants A and B respectively on which the rate of reaction depends.

- (i) Rate of chemical reaction is directly proportional to the concentration of the reactants.
- (ii) The rate law represents the experimentally observed rate of reaction, which depends upon the slowest step of the reaction.
- (iii) Rate law cannot be deduced from the relationship for a given equation. It can be found by experiment only.

- 3.3 Rate constant :** Consider a simple reaction,  $A \rightarrow B$ . If  $C_A$  is the molar concentration or active mass of A at a particular instant, then,  $\frac{dx}{dt} \propto C_A$  or  $\frac{dx}{dt} = kC_A$ ; Where k is a **proportionality constant**, called **velocity constant** or **rate constant** or **specific rate of a reaction**.

At a fixed temperature, if  $C_A = 1$ , then  $\text{Rate} = \frac{dx}{dt} = k$

"Rate of a reaction at unit concentration of reactants is called rate constant."

(i) The value of rate constant depends on, Nature of reactant, Temperature and Catalyst

(It is independent on concentration of the reactants)

(ii) Unit of rate constant :  $\left[\frac{\text{litre}}{\text{mol}}\right]^{n-1} \times \text{sec}^{-1}$  or  $= \left[\frac{\text{mol}}{\text{litre}}\right]^{1-n} \times \text{sec}^{-1}$

Where n = order of reaction

### 3.4 Difference between Rate law and Law of mass action

<i>Rate law</i>	<i>Law of mass action</i>
It is an experimentally observed law.	It is a theoretical law.
It depends on the concentration terms on which the rate of reaction actually depends	It is based upon the stoichiometry of the equation
Example for the reaction, $aA + bB \rightarrow \text{Product}$	Example for the reaction, $aA + bB \rightarrow \text{Products}$
Rate = $k [A]^m [B]^n$	Rate = $k [A]^a [B]^b$

### 3.5 Difference between Rate of reaction and Rate constant

<i>Rate of reaction</i>	<i>Rate constant</i>
It is the speed with which reactants are converted into products.	It is proportionality constant.
It is measured as the rate of decrease of the concentration of reactants or the rate of increase of concentration of products with time.	It is equal to rate of reaction when the concentration of each of the reactants is unity.
It depends upon the initial concentration of the reactants.	It is independent of the initial concentration of the reactants. It has a constant value at fixed temperature.

## 4. ORDER OF REACTION

The order of a reaction may be defined as the sum of the powers to which conc. terms must be raised in an experimentally determined rate equation :

For the reaction :  $aA + bB \rightarrow \text{product}$

Experimental rate equation :  $r = k [A]^m [B]^n$

order with respect to A = m

order with respect to B = n

Total order = m + n

m and n may or may not be equal to a and b.

**Note :** Order may be zero, fractional, integer or negative.

**Example :**

Reaction	Experimental rate equation	order
$\text{H}_2 + \text{Cl}_2 \rightarrow 2\text{HCl}$	$r = k$	zero
$\text{H}_2 + \text{Br}_2 \rightarrow 2\text{HBr}$	$r = k [\text{H}_2] [\text{Br}_2]^{1/2}$	one and half
$\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI}$	$r = k [\text{H}_2] [\text{I}_2]$	two

**Examples of fractional order reaction**

**Reaction :**  $\text{CO(g)} + \text{Cl}_2\text{(g)} \rightarrow \text{COCl}_2\text{(g)}$   
 $v = k [\text{CO}]^2 [\text{Cl}_2]^{1/2}$ , order = 2.5

**Reaction :**  $\text{COCl}_2\text{(g)} \rightarrow \text{CO(g)} + \text{Cl}_2\text{(g)}$   
 $v = k [\text{COCl}_2]^{3/2}$ , order = 1.5

**Illustration**

1. The dimensions of rate constant of a second order reaction involves :  
 (A) time and concentration (B) neither time nor concentration  
 (C) time only (D) concentration only

**Ans.** (A)

**Sol.**  $k = \frac{\text{Rate}}{[\text{A}]^2} = \frac{\text{mol L}^{-1}\text{s}^{-1}}{(\text{mol L}^{-1})^2} = \frac{\text{s}^{-1}}{\text{mol L}^{-1}} = (\text{mol L}^{-1})^{-1} \text{s}^{-1}$

2. The rate constant of a reaction has same units as the rate of reaction. The reaction is of  
 (A) zero order (B) first order (C) second order (D) none of these

**Ans.** (A)

**Sol.** For a zero order reaction,  $r = k[\text{A}]^0$ . Thus the units of  $k$  are the same as that of rate of reaction.

3. On which of the following factors, the rate constant does not depend ?  
 (A) Temperature (B) Concentration (C) Presence of catalyst (D) Nature of reactants

**Ans.** (A)

**Sol.** Rate constant is independent of the conc. of the reactants.

**Exercise**

The rate constant of  $n^{\text{th}}$  order has units

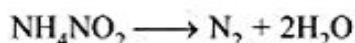
(A)  $\text{litre}^{1-n} \text{mol}^{1-n} \text{sec}^{-1}$  (B)  $\text{mol}^{1-n} \text{litre}^{1-n} \text{sec}$  (C)  $\text{mol}^{1-n} \text{litre}^n \text{sec}^{-1}$  (D)  $\text{mol}^{1-n} \text{litre}^{n-1} \text{sec}^{-1}$

**Ans.** (D)

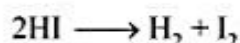
**5. MOLECULARITY**

The number of reacting species (atoms, ions or molecules) taking part in an elementary reaction, which must collide simultaneously in order to bring about a chemical reaction is called molecularity of a reaction. The reaction can be unimolecular when one reacting species is involved, for example, decomposition of ammonium nitrite.

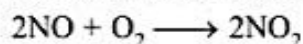




Bimolecular reactions involve collision between two species, for example, dissociation of hydrogen iodine.



Trimolecular reactions involve simultaneous collision between three reacting species, for example,



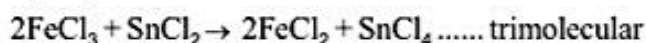
### Molecularity of a reaction is :

- (i) Always a whole number (not zero) and never a fraction.
- (ii) The probability that more than three molecules can collide and react simultaneously is very small. Hence, the molecularity greater than three is not observed.

Thus, from the above discussion we can conclude the following:

- (a) Order of a reaction is an experimentally determined quantity. It can be zero and even a fraction but molecularity cannot be zero or a non integer.
- (b) Order is defined to elementary as well as complex reactions whereas molecularity is defined only for elementary reactions. For complex reaction molecularity has no meaning.
- (c) For an elementary reaction order and molecularity are same.

### Example



**Note :** If the reaction takes place in two or more steps then the overall molecularity of the reaction is monitored by the slow or rate determining step.

## 5.1 Difference Between Molecularity and Order of Reaction

Molecularity	Order of Reaction
1. Molecularity can neither be zero nor fractional	Order of a reaction can be zero, fractional or integer
2. It is independent of pressure and temperature	It depends upon pressure and temperature
3. It is assigned for each step of mechanism separately	It is assigned for overall reaction as well as each step of reaction.
4. It is the number of molecules of reactants concentration terms taking part in elementary step of a reaction.	It is sum of power raised to the concentration of the rate expression.
5. Molecularity of reaction cannot be negative	Order of a reaction may have negative value.

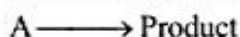


## 6. INTEGRATED RATE LAWS FOR DIFFERENT ORDER OF REACTIONS

Differential rate law ( $\text{rate} = \frac{dx}{dt} = K[\text{Conc.}]^n$ ) expressed the dependance of rate of reaction on concentration of reactants. Upon integrating the differential rate law, we get integrated rate law expression which is a concentration-time equation from which we can calculate concentration at any time (t) or the time required for an initial concentration to reach any particular value. The integrated rate law expression for different reactions have been discussed below :

**6.1 Zero order reaction :** Reaction whose rate is not affected by concentration or in which the concentration of reactant do not change with time are said to be of zero order reaction.

**Calculation of Rate Constant :** Let us take the reaction



conc. at  $t = 0$      $a$                        $0$

$$\frac{dx}{dt} = k[A]^0, \quad \frac{dx}{dt} = k; \quad dx = k \, dt$$

$$\text{or, } \int_0^x dx = \int_0^t k \, dt$$

conc. of A at, time  $t = 0$  is  $[A]_0 = a$  (say)

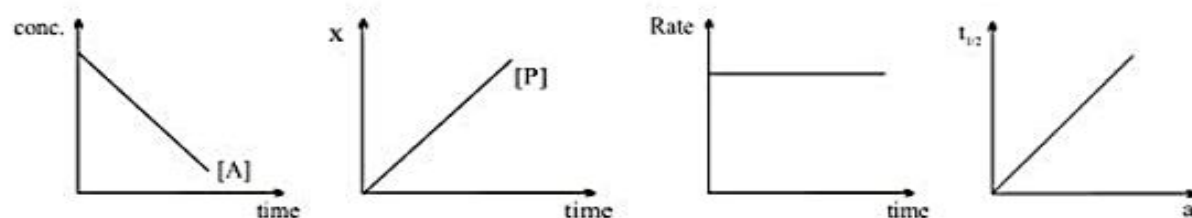
Integrated rate equation,  $k = \frac{x}{t}$  ; The rate of reaction is independent of the concentration of the reacting substance.

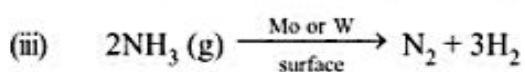
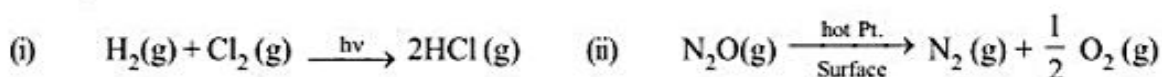
**Half life period of zero order reaction :** When  $t = t_{1/2}$ ;  $x = \frac{a}{2}$ ;  $t_{1/2} = \frac{a}{2k}$  or  $t_{1/2} \propto a$  ; The half life period is directly proportional to the initial concentration of the reactants.

**Unit of Rate constant :**  $= \frac{\text{mole}}{\text{lit. sec.}}$  ; Unit of rate of reaction = Unit of rate constant.

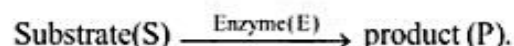
**Characteristics of zero order reactions:**

- (i) Concentration of reactant decreases linearly with time.
- (ii) Unit of  $k$  is  $\text{mol l}^{-1} \text{time}^{-1}$ .
- (iii) Time required for the 100% completion of reaction is  $\frac{[A]_0}{k}$
- (iv)  $t_{1/2} = \frac{[A]_0}{2k}$
- (v) Zero order reaction must be a complex reaction
- (vi) Graph related with zero order reactions.



**Examples :**

(iv) Enzyme catalysed reaction

**Illustration**

The rate constant for a zero order reaction is  $2 \times 10^{-2} \text{ mol L}^{-1}\text{sec}^{-1}$ , if the concentration of the reactant after 25 sec is 0.25 M, calculate the initial concentration.

Ans. 0.75 M

Sol.  $2 \times 10^{-2} \times 25 = [A_0 - 0.25]$ 

$$0.5 = A_0 - 0.25 \quad \therefore A_0 = 0.75$$

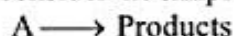
**Exercise**

A certain substance A is mixed with an equimolar quantity of substance B. At the end of an hour A is 75% reacted. Calculate the time when A is 10% unreacted. (Given: order of reaction is zero)

Ans. 1.2 hr

**6.2 First order reactions**For the reaction :  $A \longrightarrow \text{Products}$ Rate of reaction  $\propto [A]$ .For the reaction :  $2A \longrightarrow \text{Products}$ Rate of reaction  $\propto [A]$  only.For the reaction :  $A + B \longrightarrow \text{Products}$ Rate of reaction  $\propto [A]$  or  $[B]$  only.

Let us consider the simplest case viz.



Suppose we start with 'a' moles per litre of the reactant A. After time t, suppose x moles per litre of it, have decomposed. Therefore, the concentration of A after time t = (a - x) moles per litre. Then according to Law of Mass Action.

Rate of reaction  $\propto (a - x)$ 

$$\text{i.e., } \frac{dx}{dt} \propto (a - x) \quad \text{or} \quad \frac{dx}{dt} = k(a - x) \quad \dots (1)$$

where k is called the rate constant or the specific reaction rate for the reaction of the first order.

The expression for the rate constant k may be derived as follows :

Equation (1) may be rewritten in the form

$$\frac{dx}{a - x} = k dt \quad \dots (2)$$

Integrating equation (2), we get  $\int \frac{dx}{a-x} = \int k dt$

$$\text{or} \quad k = \frac{1}{t} \ln \frac{a}{a-x} \quad \dots\dots(3)$$

$$\text{or} \quad k = \frac{2.303}{t} \log \frac{a}{a-x} \quad \dots\dots(4)$$

Equation (4) is sometimes written in another form which is obtained as follows :

If the initial concentration is  $[A]_0$  and the concentration after time  $t$  is  $[A]$ , then putting  $a = [A]_0$  and  $(a-x) = [A]$  equation (iv) becomes

$$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]} \quad \dots\dots (5)$$

Further, putting  $a = [A]_0$  and  $(a-x) = [A]$  in eqn. (3), we get

$$kt = \ln \frac{[A]_0}{[A]}$$

which can be written in the exponential form as

$$\frac{[A]_0}{[A]} = e^{kt} \text{ or } \frac{[A]}{[A]_0} = e^{-kt}$$

$$\text{or} \quad [A] = [A]_0 e^{-kt} \quad \dots\dots (6)$$

### Characteristics of First Order Reaction :

- (i) Unit of rate constant is  $\text{time}^{-1}$ .
- (ii)  $t_{1/2} = \frac{0.693}{k}$  (Half-life)
- (iii)  $\log(a-x)$  v/s  $t$  is a straight line with slope  $-\frac{k}{2.303}$ .
- (iv) Graph related with first order reactions.



### Examples:

- (i) Radioactive disintegration is a first order reaction.
- (ii) 
$$\text{C}_{12}\text{H}_{22}\text{O}_{11} + \text{H}_2\text{O} \xrightarrow[\text{Inversion}]{\text{H}^+ \text{ catalysed hydrolysis}} \text{C}_6\text{H}_{12}\text{O}_6 + \text{C}_6\text{H}_{12}\text{O}_6$$
  
(glucose) (fructose)
- (iii) Mineral acid catalyzed hydrolysis of esters.
- (iv) Decomposition of  $\text{H}_2\text{O}_2$  in aqueous solution.

**Illustration**

1. A reaction which is of first order with respect to reactant 'A' has a rate constant of  $6.0 \text{ min}^{-1}$ . If we start with  $[A] = 0.5 \text{ mol L}^{-1}$ , when will  $[A]$  reach the value of  $0.05 \text{ mol L}^{-1}$ .

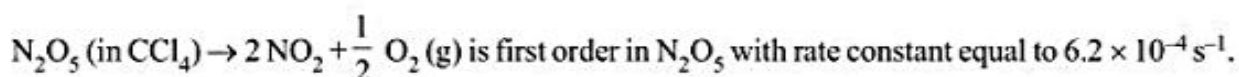
(A) 0.384 min (B) 0.15 min (C) 3 min (D) 3.84 min

Ans. (A)

Sol.  $t = \frac{2.303}{k} \log \frac{a}{a-x}$

Or  $t = \frac{2.303}{6} \log \frac{0.5}{0.05} = \frac{2.303}{6} \log 10 = \frac{2.303}{6} = 0.384 \text{ min.}$

2. The reaction



What is the value of rate of reaction when  $[\text{N}_2\text{O}_5] = 1.25 \text{ mol L}^{-1}$ ?

(A)  $7.75 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$  (B)  $6.35 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$   
(C)  $5.15 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}$  (D)  $3.85 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$

Ans. (A)

Sol. Reaction rate  $= k [\text{N}_2\text{O}_5] = 6.2 \times 10^{-4} \cdot 1.25 = 7.75 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$

3. A first order reaction is 20 % completed in 10 minutes. Calculate the time taken for the reaction to go to 80 % completion.

Sol. Applying first order equation,

$$k = \frac{2.303}{t} \log_{10} \frac{100}{(100-20)} = \frac{2.303}{10} \log_{10} \frac{100}{80} = 0.0223 \text{ min}^{-1}$$

Again applying first order equation,

$$t = \frac{2.303}{k} \log_{10} \frac{100}{(100-80)} = \frac{2.303}{0.0223} \log_{10} \frac{100}{20} = 72.18 \text{ min}$$

4. The rate of the first order reaction  $\text{X} \rightarrow \text{products}$  is  $7.5 \times 10^{-4} \text{ mol L}^{-1} \text{ min}^{-1}$ . What will be the value of rate constant when the concentration of X is  $0.5 \text{ mol L}^{-1}$ ?

(A)  $3.75 \times 10^{-4} \text{ s}^{-1}$  (B)  $2.5 \times 10^{-5} \text{ s}^{-1}$  (C)  $1.5 \times 10^{-3} \text{ s}^{-1}$  (D)  $8.0 \times 10^{-4} \text{ s}^{-1}$

Ans. (B)

Sol. Rate of reaction  $= 7.5 \times 10^{-4} \text{ mol L}^{-1} \text{ min}^{-1}$

$$= \frac{7.5 \times 10^{-4}}{60} \text{ mol L}^{-1} \text{ s}^{-1} = 1.25 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}$$

Rate of reaction  $= k [\text{concentration. of reactant X}]$

Or  $k = \frac{1.25 \times 10^{-5}}{0.5} = 2.5 \times 10^{-5} \text{ s}^{-1}$



**Exercise**

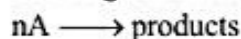
In a first order reaction, the concentration of the reactants is reduced to 25% in 1 hour. The half life period of the reaction is

- (A)  $2h$                       (B)  $4h$                       (C)  $\frac{1}{2}h$                       (D)  $\frac{1}{4}h$

Ans. (C)

### 6.3 Second Order Reaction :

(i) For the given reaction.



Differential rate equation  $\frac{dx}{dt} = k(a-x)^2$

Integrated rate equation  $k = \frac{1}{t} \cdot \frac{x}{a(a-x)}$  or  $kt = \frac{1}{a-x} - \frac{1}{a}$ .

Is the above rate constant w.r.t. reaction or disappearance.

(ii) For the given reaction.



at time  $t = 0$        $a$        $b$

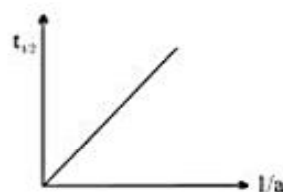
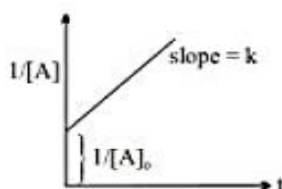
at time  $t = t$        $a-x$        $b-x$

differential rate equation  $\frac{dx}{dt} = k(a-x)(b-x)$ .

Integrated rate equation  $k = \frac{2.303}{t(a-b)} \log_{10} \frac{b(a-x)}{a(b-x)}$

### Characteristics of Second Order Reaction :

- (i) Unit of rate constant  $L \text{ mol}^{-1} \text{ time}^{-1}$ .
- (ii)  $t_{1/2} \propto a^{-1}$  (In general  $t_{1/2} \propto a^{(1-n)}$ ;  $n$  = order of reactions).
- (iii) 2<sup>nd</sup> order reaction conforms to first order when one of the reactant is in excess.



### Examples:

- (i) Saponification (hydrolysis of esters catalysed with alkali).  
 $\text{CH}_3\text{COOC}_2\text{H}_5 + \text{NaOH} \longrightarrow \text{CH}_3\text{COONa} + \text{C}_2\text{H}_5\text{OH}$
- (ii) Hydrogenation of ethane  $\text{C}_2\text{H}_4 + \text{H}_2 \xrightarrow{100^\circ\text{C}} \text{C}_2\text{H}_6$ .
- (iii)  $2 \text{O}_3 \longrightarrow 3 \text{O}_2$ .

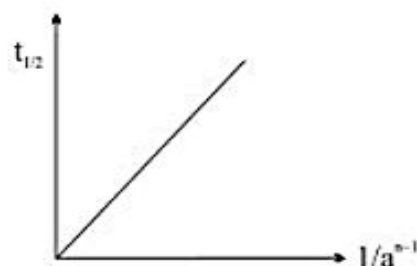
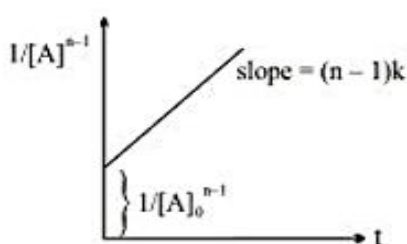
#### 6.4 $n^{\text{th}}$ Order reaction

Consider the reaction



$$k^{\dagger} = \frac{1}{n-1} \left\{ \frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}} \right\} \quad [n \neq 1, n = \text{order}]$$

$$t_{1/2} = \frac{1}{k(n-1)} \left[ \frac{2^{n-1}-1}{a^{n-1}} \right]$$



What is the 'k' involved in the rate law rate constant w.r.t. reaction or w.r.t. disappearance

### 7. METHODS OF DETERMINATION OF ORDER OF REACTIONS

A few methods commonly used are given below :

- (i) **Hit & Trial Method** : It is method of using integrated rate equations, where the experimental values of  $a$ ,  $x$  &  $t$  are put into these equations. One which gives a constant value of  $k$  for different sets of  $a$ ,  $x$  &  $t$  correspond to the order of the reaction.
- (ii) **Graphical Method** :
  - (i) A plot of  $\log(a-x)$  versus ' $t$ ' gives a straight line for the First order reaction.
  - (ii) A plot of  $(a-x)^{-(n-1)}$  versus ' $t$ ' gives a straight line for any reaction of the order  $n$  except  $n = 1$ .
- (iii) **Half Life Method** : The half life of  $n^{\text{th}}$  order reaction is given by  $t_{1/2} \propto 1/a^{n-1}$   
 By experimental observation of the dependence of half life on initial concentration we can determine  $n$ , the order of reaction. 
$$n = 1 + \frac{\log(t_{1/2})_2 - \log(t_{1/2})_1}{\log(a_0)_1 - \log(a_0)_2}$$
- (iv) **Initial rate method**. Initial rate method is used to determine the order of reaction in cases where more than one reactant is used. It involves the determination of the order of different reactants separately. A series of experiments are performed in which concentration of one particular reactant is varied whereas conc. of other reactants are kept constant. In each experiment the initial rate is determined from the plot of conc. vs. time, e.g., if conc. of  $A$  is doubled, and initial rate of reaction is also doubled, order of reaction w.r.t  $A$  is 1.

### Illustration

1. The following result have been obtained during kinetic studies of the reaction.



Experiment	[A]/M	[B]/M	Initial rate of formation of D / M sec <sup>-1</sup>
I	0.1	0.1	$6.0 \times 10^{-3}$
II	0.3	0.2	$7.2 \times 10^{-2}$
III	0.3	0.4	$2.88 \times 10^{-1}$
IV	0.4	0.1	$2.40 \times 10^{-2}$

- (i) Determine the rate law of above reaction  
 (ii) Find the rate constant of above reaction in (mole/L)<sup>1-n</sup> sec<sup>-1</sup>

**Sol.**  $r_1 = 6 \times 10^{-3} = k [A]^m [B]^n$   
 $6 \times 10^{-3} = k [0.1]^m [0.1]^n$  .....(i)  
 $r_2 = 7.2 \times 10^{-2} = k (0.3)^m (0.2)^n$  .....(ii)  
 $r_3 = 2.88 \times 10^{-1} = k (0.3)^m (0.4)^n$  .....(iii)  
 $r_4 = 2.40 \times 10^{-2} = k (0.4)^m (0.1)^n$  .....(iv)

eg. (iii)/(ii)  $\frac{2.88}{0.72} = 4 = \left(\frac{0.4}{0.2}\right)^n = 2^n \Rightarrow n = 2$

doing (iv)/(i)  $\frac{2.40}{0.6} = (4)^m$

$\Rightarrow m = 1$

rate law =  $-\frac{d[A]}{dt} = k [A]^1 [B]^2$  ;  $k = \frac{6 \times 10^{-3}}{10^{-3}} = 6 \text{ M}^{-2} \text{ sec}^{-1}$

2. The catalytic decomposition of N<sub>2</sub>O by gold at 900°C and at an initial pressure of 200 mm is 50% complete in 53 minutes and 73% complete in 100 minutes.

- (i) What is the order of the reaction?  
 (ii) Calculate the rate constant.  
 (iii) How much of N<sub>2</sub>O will decompose in 100 min. at the same temperature but at initial pressure of 600 mm?  
**[2021013194]**

**Ans.** (i) first order (ii)  $k = 1.308 \times 10^{-2} \text{ min}^{-1}$  (iii) 73%

**Sol.** N<sub>2</sub>O  $\longrightarrow$  Product

$$K = \frac{1}{t} \ln \frac{A_0}{A_t}$$

$$= \frac{1}{53} \ln \frac{A_0}{A_{0/2}} = \frac{\ln 2}{53}$$

$$= \frac{1}{100} \ln \frac{100}{27}$$

order = 1<sup>st</sup> order

$$K = \frac{\ln 2}{53}$$

$$X\% = \frac{600 \times 73}{100} = 6 \times 73 \text{ mmHg}$$

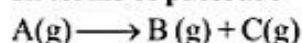
### Exercise

The half life period of decomposition of a compound is 50 minutes. If the initial concentration is halved, the half life period is reduced to 25 minutes. What is the order of reaction?

**Ans.** Zero order

## 8. CALCULATION OF FIRST ORDER RATE CONSTANT USING DIFFERENT PARAMETERS

### (I) In terms of pressure



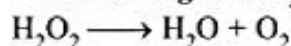
$$k = \frac{2.303}{t} \log \frac{P_0}{2P_0 - P_T}$$

where

$P_0$  = Initial partial pressure of A

$P_T$  = Total pressure of gaseous system at time 't'

### (II) Decomposition of $H_2O_2$ in aqueous solution (In terms of volume of reagent $KMnO_4$ required in titration against $H_2O_2$ ).



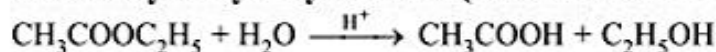
$$k = \frac{2.303}{t} \log \frac{V_0}{V_t}$$

where

$V_0$  = Volume of  $KMnO_4$  required in titration of  $H_2O_2$  sample taken initially

$V_t$  = Volume of  $KMnO_4$  required in titration of same volume of  $H_2O_2$  sample at time 't'.

### (III) Acid catalysed hydrolysis of ester (In terms of volume of reagent NaOH required in titration)



NaOH reacts with  $H^+$  and  $CH_3COOH$ .

$$k = \frac{2.303}{t} \log \left( \frac{V_\infty - V_0}{V_\infty - V_t} \right)$$

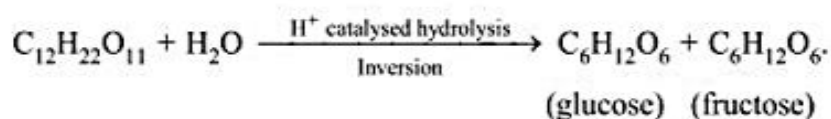
where

$V_0$  = volume of NaOH required in titration when reacted with  $H^+$  (at start)

$V_t$  = volume of NaOH required in titration when reacted with  $H^+$  and  $CH_3COOH$  at time 't'.

$V_\infty$  = volume of NaOH required in titration when reaction is completed



**(IV) Inversion of cane sugar (In terms of angle of rotation)**

$$k = \frac{2.303}{t} \log \left( \frac{r_0 - r_\infty}{r_t - r_\infty} \right)$$

where

$r_0$  = initial angle of rotation of the sample

$r_t$  = angle of rotation after time  $t$

$r_\infty$  = angle of rotation after completion of reaction

**(V) Oxide layer formation:**

$$k = \frac{1}{t} \ln \frac{\tau_{\max}}{\tau_{\max} - \tau}$$

where

$\tau_{\max}$  = Thickness of oxide layer after  $\infty$  times

$\tau$  = Thickness of oxide layer at time ' $t$ '.

**(VI) Bacterial Growth:**

$$k = \frac{1}{t} \ln \frac{a+x}{a}$$

**Illustration**

1. From the following data show that decomposition of  $\text{H}_2\text{O}_2$  in aqueous solution is first order.

Time (in minutes)	0	10	20
Volume (in c.c. of $\text{KMnO}_4$ )	22.8	13.3	8.25

**Ans.** First order

**Sol.**  $K = \frac{2.303}{t} \log \frac{v_0}{v_t}$

$$K_1 = \frac{2.303}{t} \log \frac{22.8}{13.3} = 0.05$$

$$K_2 = \frac{2.303}{t} \log \frac{22.8}{8.25} = 0.05$$

$\therefore$  It is first order reaction

2. The following data were obtained in experiment on inversion of cane sugar.

Time (minutes)	0	60	120	180	360	$\infty$
Angle of rotation (degree)	+13.1	+11.6	+10.2	+9.0	+5.87	-3.8

Show that the reaction is of first order. After what time would you expect a zero reading in polarimeter?

**Ans.** 966 min

**Sol.**  $K = \frac{2.303}{t} \log \frac{r_0 - r_\infty}{r_t - r_\infty}$

$$K_1 = \frac{2.303}{60} \log \frac{13.1 + 3.8}{11.6 + 3.8} = 0.00155$$

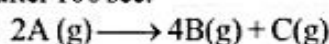
$$K_2 = 0.001566 \quad (K_1 = K_2)$$

∴ It is first order reaction

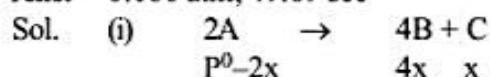
$$t = \frac{2.303}{0.001566} \log \frac{13.1 + 3.8}{0 + 3.8}$$

$$t \approx 966 \text{ min}$$

3. The reaction given below, rate constant for disappearance of A is  $7.48 \times 10^{-3} \text{ sec}^{-1}$ . Calculate the time required for the total pressure in a system containing A at an initial pressure of 0.1 atm to rise to 0.145 atm and also find the total pressure after 100 sec.



**Ans.** 0.180 atm, 47.69 sec



$$t = \frac{2.303}{7.48 \times 10^{-3}} \log \frac{0.1}{0.1 - 0.3} = 47.815$$

(ii) 
$$\frac{100 \times 7.48 \times 10^{-3}}{2.303} = \log \frac{0.1}{y}$$

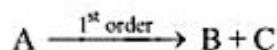
$$y = 0.04732$$

$$a - 2x = 0.1 - 2x$$

$$x = 0.02634$$

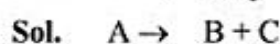
$$P_t = P^0 + 3x = 0.18 \text{ atm}$$

4. In this case we have

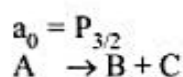


Time	t	∞
Total pressure of A + B + C	$P_2$	$P_3$
Find k.		

**Ans.**  $k = \frac{1}{t} \ln \frac{P_3}{2(P_3 - P_2)}$



At infinite  $P_3$  it means initially P of A is  $P_{3/2}$  which converts into B and C  $\left[ \frac{P_3}{2} + \frac{P_3}{2} = P_3 \right]$



$$\frac{P_3}{2} - x = x$$

$$\frac{P_3}{2} + x = P_2$$

$$x = P_2 - \frac{P_3}{2}$$

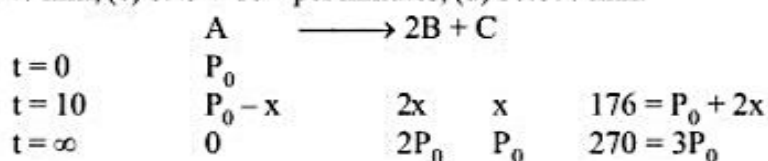
$$k = \frac{1}{t} \ln \frac{P_3/2}{P_3/2 - P_2 + \frac{P_3}{2}} = \frac{1}{t} \ln \frac{P_3}{2(P_3 - P_2)}$$

5. At 100°C the gaseous reaction  $A \longrightarrow 2B + C$  was observed to be of first order. On starting with pure A it is found that at the end of 10 minutes the total pressure of system is 176 mm. Hg and after a long time 270 mm Hg. From these data find (a) initial pressure of A (b) the pressure of A at the end of 10 minutes (c) the specific rate of reaction and (d) the half life period of the reaction?

Given :  $\ln\left(\frac{90}{47}\right) = 0.65$

Ans. (a) 90 mm, (b) 47 mm, (c)  $6.49 \times 10^{-2}$  per minutes, (d) 10.677 min.

Sol.



(a)  $P_0 = \frac{270}{3} = 90$

$$x = \frac{176 - 90}{2} = 43$$

(c)  $K = \frac{1}{10 \times 60} \ln \frac{90}{90 \times 43}$

(d)  $t_{1/2} = \frac{\ln 2}{K}$

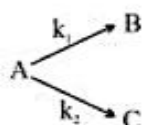
### Exercise

The reaction  $AsH_3(g) \longrightarrow As(s) + \frac{3}{2} H_2(g)$  was followed at constant volume at 310°C by measuring the gas pressure at intervals Show from the following figures that reaction is of first order.

Time (in hrs)	0	5	7.5	10
Total pressure (in mm)	758	827	856	882

Ans. First order

## 9. ELEMENTARY PARALLEL PATH REACTIONS



Let the initial concentration of A be  $[A]_0$  and let after time  $t$ , the concentrations of A, B and C be  $[A]$ ,  $[B]$  and  $[C]$ , respectively. It is obvious that

$$[A]_0 = [A] + [B] + [C]$$

The differential rate expressions are

$$\frac{d[B]}{dt} = k_1 [A]$$

$$\frac{d[C]}{dt} = k_2 [A] \quad , \quad \frac{[B]}{[C]} = \frac{k_1}{k_2}$$

The overall-rate of disappearance of A is given as

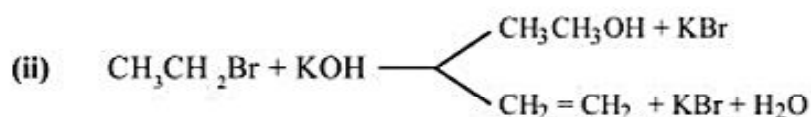
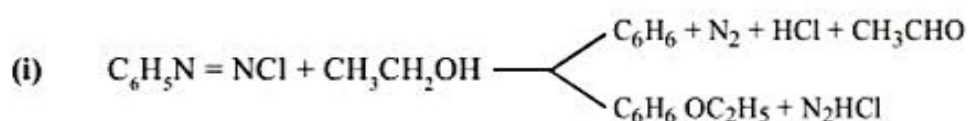
$$-\frac{d[A]}{dt} = [k_1 + k_2] [A]$$

$$[k_1 + k_2] t = \ln \frac{[A]_0}{[A]_t}$$

$$\% \text{ of B in products} = \frac{k_1}{k_1 + k_2} \times 100$$

$$\% \text{ of C in products} = \frac{k_2}{k_1 + k_2} \times 100$$

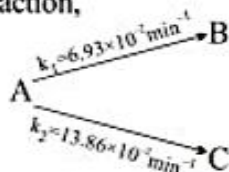
### Some examples of parallel reactions





**Illustration**

1. Consider the reaction,



A, B and C all are optically active compound. If optical rotation per unit concentration of A, B and C are  $60^\circ$ ,  $-72^\circ$ ,  $42^\circ$  and initial concentration of A is 2 M then select write statement (s).

- (A) Solution will be optically active and dextro after very long time  
 (B) Solution will be optically active and levo after very long time  
 (C) Half life of reaction is 15 min  
 (D) After 75% conversion of A into B and C angle of rotation of solution will be  $36^\circ$ .

**Ans.** (A), (D)

**Sol.** After very long time concentration of B =  $\frac{1}{3} \times 2$

$$\text{After very long time concentration of C} = \frac{2}{3} \times 2 \Rightarrow \frac{4}{3}$$

$$\text{Angle of rotation after reaction} = \frac{2}{3} \times (-72) + \frac{4}{3} \times 42 \Rightarrow 8^\circ$$

$$(t_{1/2})_1 = \frac{0.693}{6.93 \times 10^{-2}} = 10 \text{ min}$$

$$(t_{1/2})_2 = \frac{0.693}{13.86 \times 10^{-2}} = 5 \text{ min}$$

$$\therefore k_{\text{overall}} = k_1 + k_2$$

$$\left( \frac{1}{t_{1/2}} \right)_{\text{overall}} = \left( \frac{1}{t_{1/2}} \right)_1 + \left( \frac{1}{t_{1/2}} \right)_2$$

$$t_{\text{overall}} = \frac{10}{3} \text{ min.}$$

After 75% conversion of A into B and C  
 Concentration of A = 0.5 M

$$\text{Concentration of B} = \frac{1}{3} \times 1.5 \Rightarrow 0.5 \text{ M}$$

$$\text{Concentration of C} = \frac{2}{3} \times 1.5 \Rightarrow 1 \text{ M}$$

$$\therefore \text{Angle of rotation} = 0.5 \times 60^\circ + 42^\circ \times 1 - 72^\circ \times 0.5 \Rightarrow 36^\circ]$$

2.  $A \begin{cases} \xrightarrow{k_1} B \\ \xrightarrow{k_2} C \end{cases}$   $k_1 = x \text{ hr}^{-1}; k_1 : k_2 = 1 : 10$ . Calculate  $\frac{[C]}{[A]}$  after one hour from the start of the reaction.

Assuming only A was present in the beginning.

Ans.  $\frac{[C]}{[A]} = \frac{10}{11}(e^{11x} - 1)$

Sol.  $\frac{k_1}{k_2} = \frac{1}{10}$

$$k_1 = x \quad k_2 = k_1 \times 10 = x \times 10$$

$$k_1 + k_2 = x + 10x = 11x$$

$$\frac{[B]}{[C]} = \frac{1}{10} \Rightarrow B_t = \frac{[C_t]}{10}$$

For parallel reaction

$$-\frac{d[A]}{dt} = [k_1 + k_2] A$$

$$\ln \frac{[A_0]}{[A_t]} = (k_1 + k_2) t$$

$$\ln \frac{[A_t + B_t + C_t]}{A_t} = (k_1 + k_2) t$$

$$\ln \left[ \frac{A_t + \frac{C_t}{10} + C_t}{A_t} \right] = (k_1 + k_2) t \quad \Rightarrow \quad \ln \left[ 1 + \frac{11C_t}{10A_t} \right] = (x + 10x) t$$

$$1 + \frac{11C_t}{10A_t} = e^{11x} \quad \because (t = 1 \text{ hr given})$$

$$\frac{[C_t]}{[A_t]} = (e^{11x} - 1) \frac{10}{11}$$

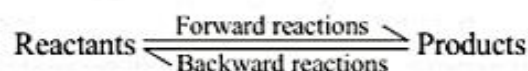
### Exercise

For a reaction  $x \begin{cases} \xrightarrow{k_1} y \\ \xrightarrow{k_2} z \end{cases}$ , calculate value of ratio,  $\frac{[x]_t}{[y] + [z]}$  at any given instant t.

Ans.  $\frac{1}{e^{(K_1+K_2)t} - 1}$

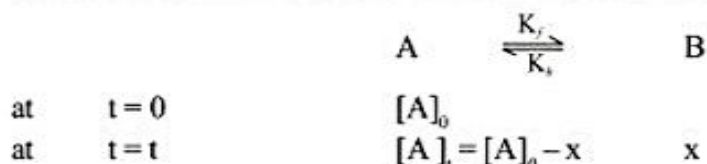
## 10. REVERSIBLE OR OPPOSING REACTIONS

Reversible reactions are these in which products formed converted back into reactants simultaneously.



### Kinetics of reversible reactions (First order opposed by first order) :

Consider a reversible reaction in which forward and backward reactions follow first order.



$K_f$  and  $K_b$  are rate constants of forward and backward reactions respectively.

$$\frac{dx}{dt} = K_f [A] - K_b [B]$$

$$\frac{dx}{dt} = K_f [[A]_0 - x] - K_b \cdot x \quad \text{.....(1)}$$

But at equilibrium  $\frac{dx}{dt} = 0$ ; (since concentrations become constant) and  $x$  represents  $x_{eq}$  (equilibrium concentration of B).

At equilibrium rate of forward reaction is equal to rate of backward reaction.

$$\begin{array}{l} K_f [[A]_0 - x_{eq}] = K_b \cdot x_{eq} \\ \text{or } x_{eq} = \frac{K_f [A]_0}{K_f + K_b} \quad \text{.....(2)} \end{array}$$

$$\text{Also } K_b = \frac{K_f [[A]_0 - x_{eq}]}{x_{eq}} \quad \text{.....(3)}$$

Putting values of  $x_{eq}$  and  $K_b$  in eq. (1)

$$\begin{aligned} \frac{dx}{dt} &= K_f [[A]_0 - x] - \frac{K_f [[A]_0 - x_{eq}]}{x_{eq}} \cdot x \\ &= K_f \cdot [A]_0 - K_f \cdot x - \frac{K_f [A]_0 \cdot x}{x_{eq}} + K_f \cdot x \\ \text{or, } \frac{dx}{dt} &= \frac{K_f [A]_0}{x_{eq}} [x_{eq} - x] \quad \text{.....(4)} \end{aligned}$$

On integrating the equation (4), we get

$$\text{or} \quad -\ln [x_{\text{eq.}} - x] = K_f \frac{[A]_0}{x_{\text{eq.}}} \cdot t + C \quad \text{.....(5)}$$

at  $t = 0$ ,  $x = 0$ , and  $C = -\ln x_{\text{eq.}}$

putting value of  $C$  in eq. (5)

$$\text{or} \quad -\ln [x_{\text{eq.}} - x] + \ln x_{\text{eq.}} = K_f \frac{[A]_0}{x_{\text{eq.}}} \cdot t \quad \text{.....(6)}$$

$$\text{or} \quad K_f \cdot t \cdot \frac{[A]_0}{x_{\text{eq.}}} = \ln \left[ \frac{x_{\text{eq.}}}{x_{\text{eq.}} - x} \right] \quad \text{.....(7)}$$

From eqs. (2) and (7)

$$\frac{(K_f + K_b)x_{\text{eq.}}}{[A]_0} \cdot t \cdot \frac{[A]_0}{x_{\text{eq.}}} = \ln \left[ \frac{x_{\text{eq.}}}{x_{\text{eq.}} - x} \right]$$

$$\text{or} \quad (K_f + K_b) \cdot t = \ln \left[ \frac{x_{\text{eq.}}}{x_{\text{eq.}} - x} \right] \quad \text{.....(8)}$$

$$\text{or} \quad (K_f + K_b) \cdot t = 2.303 \log \left[ \frac{x_{\text{eq.}}}{x_{\text{eq.}} - x} \right] \quad \text{.....(9)}$$

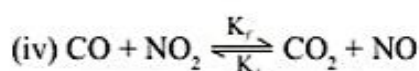
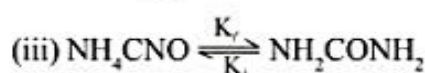
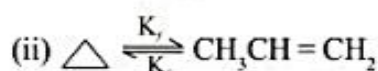
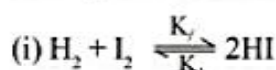
The equilibrium constant of such reversible reactions,

$$K_c = \frac{[B]_{\text{eq.}}}{[A]_{\text{eq.}}} = \frac{x_{\text{eq.}}}{[A]_0 - x_{\text{eq.}}} = \frac{K_f}{K_b}$$

If  $[B]_0$  is not equal to zero, the relation for such reversible reaction shows

$$K_f \cdot t = 2.303 \left[ \frac{[B]_0 + x_{\text{eq.}}}{[A]_0 + [B]_0} \right] \log \left[ \frac{x_{\text{eq.}}}{x_{\text{eq.}} - x} \right] \quad \text{.....(10)}$$

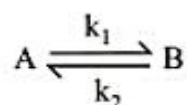
**Example of reversible reactions :**



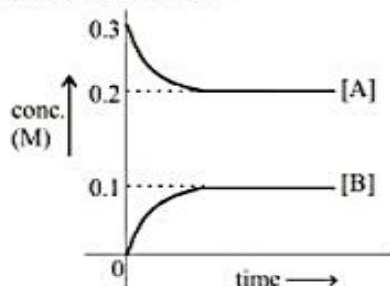


**Illustration**

Consider a reversible reaction :



Which is a first order in both the directions ( $k_1 = \frac{1.38}{3} \times 10^{-2} \text{ min}^{-1}$ ). The variation in concentration is plotted with time as shown below.



Calculate the time (in minute) at which 25 % of A would be exhausted. [ $\ln 2 = 0.69$ ]

**Sol.**  $k_{eq} = \frac{0.1}{0.2} = \frac{1}{2} = \frac{k_1}{k_2}$

$$k_2 = \frac{2}{3} \times 1.38 \times 10^{-2}$$

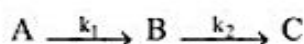
$$\ln \frac{0.1}{0.1 - 0.075} = (k_1 + k_2) t$$

$$2 \times 0.69 = 1.38 \times 10^{-2} \times t$$

$$t = 100 \text{ min.}$$

## 11. SEQUENTIAL OR CONSECUTIVE REACTIONS :

In many cases, the product formed in one of the elementary reactions acts as the reactant for some other elementary reaction. One of the examples of consecutive reactions involves the following steps.



Let the initial concentration of A be  $[A]_0$  and let after time  $t$ , the concentrations of A, B and C be  $[A]$ ,  $[B]$  and  $[C]$ , respectively. It is obvious that

$$[A]_0 = [A] + [B] + [C] \quad \dots\dots(1)$$

**Differential Rate Law :** The differential rate expressions are

$$-\frac{d[A]}{dt} = k_1[A] \quad \dots\dots(2)$$

$$\frac{d[B]}{dt} = k_1[A] - k_2[B] \quad \text{.....(3)}$$

$$\frac{d[C]}{dt} = k_2[B] \quad \text{.....(4)}$$

On integrating equation (2), we get

$$[A] = [A]_0 e^{-k_1 t} \quad \text{.....(5)}$$

Substituting [A] from equation (5) into equation (3), we get

$$\frac{d[B]}{dt} = k_1[A]_0 e^{-k_1 t} - k_2[B]$$

$$\frac{d[B]}{dt} + k_2[B] = k_1[A]_0 e^{-k_1 t}$$

**Integrated Rate Law :** Multiplying the above expression throughout by  $\exp(k_2 t)$ , we get

$$\frac{d[B]}{dt} + k_2[B]e^{k_2 t} = k_1[A]_0 e^{-(k_1 - k_2)t}$$

The left side of the above expression is equal to  $d([B]e^{k_2 t}) / dt$ . Hence, the above expression can be written as,  $d\{[B]e^{k_2 t}\} = k_1[A]_0 e^{-(k_1 - k_2)t} dt$

Integrating the above expression with  $[B] = 0$  at  $t = 0$ , we get

$$[B]e^{k_2 t} = k_1[A]_0 \left[ \frac{e^{-(k_1 - k_2)t}}{-(k_1 - k_2)} + \frac{1}{k_1 - k_2} \right]$$

$$[B] = k_1[A]_0 \left[ \frac{e^{-k_1 t}}{-(k_2 - k_1)} + \frac{e^{-k_2 t}}{k_1 - k_2} \right]$$

$$[B]_t = \frac{k_1[A]_0}{(k_2 - k_1)} [e^{-k_1 t} - e^{-k_2 t}] \quad \text{.....(6)}$$

Substituting equations (5) and (6) in equation (1), we get

$$[A]_0 = [A]_0 e^{-k_1 t} + [A]_0 \left( \frac{k_1}{k_2 - k_1} \right) (e^{-k_1 t} - e^{-k_2 t}) + [C]$$

$$\text{or } [C] = [A]_0 \left[ 1 - \frac{1}{k_2 - k_1} (k_2 e^{-k_1 t} - k_1 e^{-k_2 t}) \right] \quad \text{.....(7)}$$

Figure (1) Illustrates the general appearance of the variations of concentrations of A, B and C during the progress of the reaction.

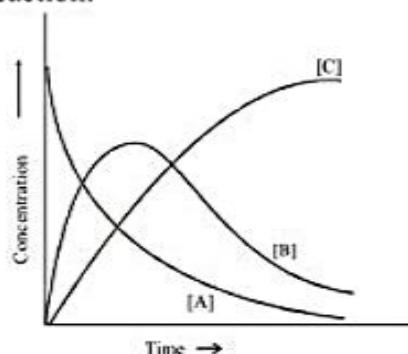


Fig. 1: Typical variations of concentration of A, B and C during the progress of the reaction  $A \rightarrow B \rightarrow C$ .

In general concentration of A decreases exponentially, the concentration of B initially increases upto a maximum and then decreases thereafter, and the concentration of C increases steadily until it reaches its final value  $[A]_0$ , when all A has changed into C.

**Maximum Concentration of B :** Equation (6) is

$$[B] = [A]_0 \left( \frac{k_1}{k_2 - k_1} \right) \{ e^{-k_1 t} - e^{-k_2 t} \}$$

At the maximum concentration of B, we have

$$\frac{d[B]}{dt} = 0$$

Hence, differentiating equation (6) with respect to t, we get

$$\frac{d[B]}{dt} = [A]_0 \left( \frac{k_1}{k_2 - k_1} \right) \{ -k_1 e^{-k_1 t} + k_2 e^{-k_2 t} \} \quad \text{.....(8)}$$

Equating equation (8) to zero, we get

$$-k_1 e^{-k_1 t_{\max}} + k_2 e^{-k_2 t_{\max}} = 0$$

$$\text{or} \quad \frac{k_1}{k_2} = e^{(k_1 - k_2)t_{\max}} \quad \text{or} \quad \ln \left( \frac{k_1}{k_2} \right) = (k_1 - k_2)t_{\max}$$

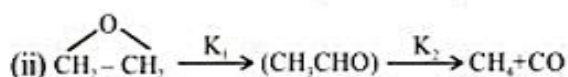
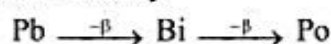
$$\text{or} \quad t_{\max} = \frac{1}{k_1 - k_2} \ln \left( \frac{k_1}{k_2} \right) \quad \text{.....(9)}$$

substituting equation (9) in equation (6), we get

$$[B]_{\max} = [A]_0 \left( \frac{k_2}{k_1} \right)^{k_2 / (k_1 - k_2)} \quad \text{.....(10)}$$

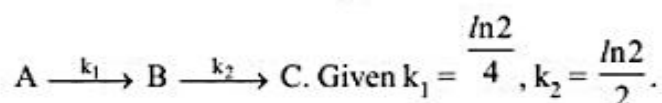
**Examples of consecutive reactions :**

(i) Several radioactive decay



**Illustration**

How much time would be required for the B to reach maximum concentration for the reaction



**Ans.**  $t = 4 \text{ min}$

**Sol.**  $k_1 = 0.173$

$k_2 = 0.3466$

$$t_{\max} = \frac{1}{k_1 - k_2} \ln \frac{k_1}{k_2} = 4 \text{ min}$$

**Exercise**

For the first order consecutive reactions.



the reaction is started with some amount of A. Match the given observation (column I) with the time (column II) related with the above reaction.

Column I (Observation)	Column II (Time)
(A) Rate of formation of C is maximum	(P) At time ' $t' = t_{1/2}$ of A (Given $k_2 = 2k_1$ )
(B) $[B]_t = [C]_t$	(Q) At time ' $t' = \frac{1}{(k_2 - k_1)} \ln \left( \frac{k_2}{k_1} \right)$
(C) $[A]_t = [B]_t$	(R) At time ' $t'$ when rate of formation of B is maximum
	(S) At time ' $t' = \frac{\ln \left( \frac{2k_1 - k_2}{k_1} \right)}{k_1 - k_2}$

**Ans.** (A) P, Q (B) R, P (C) S

**12. RATE LAW AND MECHANISM**

As already mentioned in the reaction:

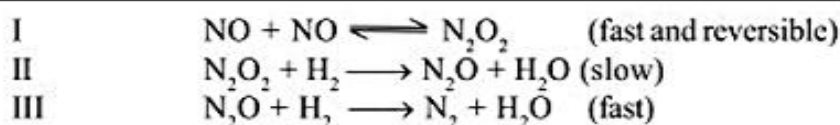


Obeys the following third order kinetics

$$\text{Rate} \propto [\text{NO}]^2 [\text{H}_2]$$

The kinetics is not in tune with chemical equation. As the law of mass action suggests each concentration term should be raised to power 2, but this is not supported by experimental facts. Under this condition we are led to believe that the reaction does not occur according to the chemical equation as written. That is the reaction is not elementary but is complicated. In order to explain the observed rate law following mechanism has been proposed.





The step II being the slowest i.e., the rate - determining step (R.D.S.). Note that the rate of formation of  $\text{N}_2$  cannot be faster than the rate of formation of  $\text{N}_2\text{O}$ . So, the rate of overall reaction or rate of formation of  $\text{N}_2$  will be equal to the rate of step II which according to law of mass action may be given as.

$$\text{Rate of overall reaction} = \text{Rate of step II} = k[\text{N}_2\text{O}_2][\text{H}_2]$$

Where  $k$  = rate constant of step II

The conc. of the intermediate ( $\text{N}_2\text{O}_2$ ) may be evaluated by applying law of mass action upon the equilibrium existing in step I as mentioned below.

$$K_c = \frac{[\text{N}_2\text{O}_2]}{[\text{NO}]^2} \quad \text{or} \quad [\text{N}_2\text{O}_2] = K_c [\text{NO}]^2$$

Putting this in the rate expression, we get

$$\text{Rate} = k \cdot k_c [\text{NO}]^2 [\text{H}_2] = k_{\text{obs}} [\text{NO}]^2 [\text{H}_2]$$

Where  $k_{\text{obs}} = k \cdot k_c$  = observed rate constant of the reaction

$$\text{Rate} \propto [\text{NO}]^2 [\text{H}_2]$$

This is the same rate - law as observed experimentally.

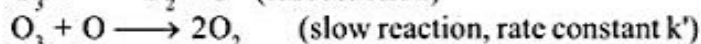
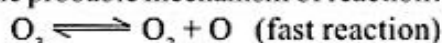
### Illustration

1. Rate law for ozone layer depletion is

$$\frac{d[\text{O}_3]}{dt} = \frac{K[\text{O}_3]^2}{[\text{O}_2]}$$

Give the probable mechanism of reaction?

**Sol.**



$$\text{Rate} = k' [\text{O}_3][\text{O}] \quad \dots (1)$$

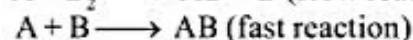
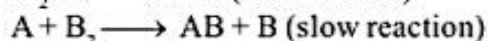
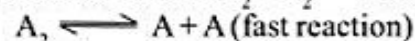
$$K_c = \frac{[\text{O}_2][\text{O}]}{[\text{O}_3]} \quad \text{or} \quad [\text{O}] = K_c \frac{[\text{O}_3]}{[\text{O}_2]}, \quad (\text{equilibrium constant } K_c)$$

putting the value in (1)

$$\text{From (1)} \quad \text{Rate} = k' \cdot [\text{O}_3] \cdot K_c \frac{[\text{O}_3]}{[\text{O}_2]} = k' \cdot K_c \cdot \frac{[\text{O}_3]^2}{[\text{O}_2]} = k \cdot \frac{[\text{O}_3]^2}{[\text{O}_2]}$$

$$k = k' \times K_c$$

2. In hypothetical reaction  $\text{A}_2 + \text{B}_2 \longrightarrow 2\text{AB}$  follows the mechanism as given below:



Give the rate law and order of reaction.

**Sol.**

Slowest step is rate determining.

$$\text{Rate} = k[\text{A}][\text{B}_2] \quad \dots (1)$$

Here  $[\text{A}]$  should be eliminated.

$$K_c = \frac{[A][A]}{[A_2]} = \frac{[A]^2}{[A_2]}$$

$$[A] = K_c^{1/2} [A_2]^{1/2}$$

$$\begin{aligned}\text{From (1). Rate} &= k K_c^{1/2} [A_2]^{1/2} [B_2] \\ &= K [A_2]^{1/2} [B_2] \\ \text{Order} &= 1 + 1/2 = 3/2\end{aligned}$$

3. For the formation of phosgene from CO(g) and chlorine,  
 $\text{CO(g)} + \text{Cl}_2\text{(g)} \longrightarrow \text{COCl}_2\text{(g)}$

The experimentally determined rate equation is,

$$\frac{d[\text{COCl}_2]}{dt} = k[\text{CO}][\text{Cl}_2]^{3/2}$$

Is the following mechanism consistent with the rate equation?

- (i)  $\text{Cl}_2 \rightleftharpoons 2\text{Cl}$  (fast)  
 (ii)  $\text{Cl} + \text{CO} \rightleftharpoons \text{COCl}$  (fast)  
 (iii)  $\text{COCl} + \text{Cl}_2 \rightleftharpoons \text{COCl}_2 + \text{Cl}$  (slow)

Sol. Multiplying equation (ii) by 2 and adding (i), we get:



$$\begin{aligned}K &= \frac{[\text{COCl}]^2}{[\text{Cl}_2][\text{CO}]^2} \\ [\text{COCl}] &= (K)^{1/2} [\text{Cl}_2]^{1/2} [\text{CO}] \quad \dots\dots (i)\end{aligned}$$

Slowest step is rate determining, hence

$$\text{Rate} = k[\text{COCl}][\text{Cl}_2] \quad \dots\dots (ii)$$

From (i) and (ii), we get

$$\begin{aligned}\text{Rate} &= kK^{1/2} [\text{Cl}_2]^{1/2} [\text{Cl}_2][\text{CO}] \\ \text{Rate} &= k'[\text{Cl}_2]^{3/2}[\text{CO}] \quad [k' = k.k^{1/2}]\end{aligned}$$

Thus, rate law is in accordance with the mechanism.

### Exercise

For the reaction  $2\text{H}_2 + 2\text{NO} \longrightarrow \text{N}_2 + 2\text{H}_2\text{O}$ , the following mechanism has been suggested:

$2\text{NO} \rightleftharpoons \text{N}_2\text{O}_2$  equilibrium constant  $K_1$  (fast)

$\text{N}_2\text{O}_2 + \text{H}_2 \xrightarrow{k_2} \text{N}_2\text{O} + \text{H}_2\text{O}$  (slow)

$\text{N}_2\text{O} + \text{H}_2 \xrightarrow{k_3} \text{N}_2 + \text{H}_2\text{O}$  (fast)

Establish the rate law for given reaction.

Ans.  $r = K [\text{NO}]^2 [\text{H}_2]$ , where  $K = k_2 \times K_1$

## 13. CATALYST

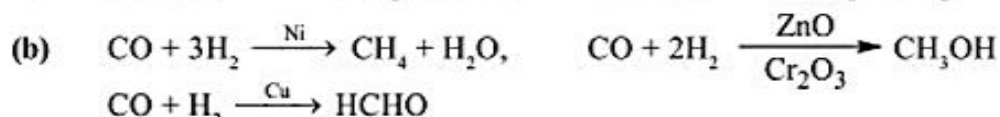
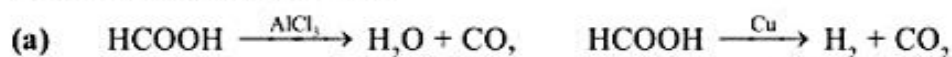
Berzelius used the term catalyst for the first time for the substances which accelerate the rate of chemical reaction. Now the term catalyst has been used for the foreign substances which influence the rate of a reaction and the phenomenon is known as catalysis. Usually two terms are used for catalysis :

**Positive Catalysis :** The phenomenon in which presence of catalyst accelerates the rate of reaction.

**Negative catalysis :** The phenomenon in which presence of catalyst retards the rate of reaction. Such substances are also known as inhibitors or negative catalyst.

### 13.1 Characteristics of Catalyst

- (i) A catalyst remains unchanged chemically at the end of reaction, however its physical state may change. e.g.  $\text{MnO}_2$  used as catalyst in granular form for the decomposition of  $\text{KClO}_3$ , is left in powder form at the end of reaction.
- (ii) A catalyst never initiate a chemical reaction. It simply influences the rate of reaction. **Exception: combination of  $\text{H}_2$  and  $\text{Cl}_2$  takes place only when moisture (catalyst) is present.**
- (iii) A small quantity of catalyst is sufficient to influence the rate of reaction e.g. 1 g atom of Platinum is sufficient to catalyse 108 litre of  $\text{H}_2\text{O}_2$  decomposition.
- (iv) A catalyst does not influence the equilibrium constant of reaction. It simply helps in attaining equilibrium earlier. It alters the rate of forward & backward reactions equally.
- (v) A catalyst normally does not alter the nature of products in a reaction. However some exceptions are found to this characteristic.



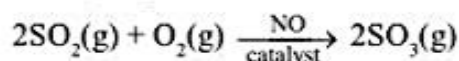
It may therefore be concluded that in some cases nature of products formed depends upon the presence and nature of catalyst used.

- (vi) A catalyst does not make reaction more exothermic
- (vii) Catalyst's activity is more or less specific : A catalyst for one reaction is not necessary to catalyse the another reaction.

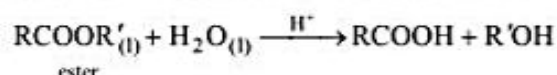
### 13.2 Types of Catalysis

- (i) **Homogeneous catalysis :** The reaction in which catalyst and the reactants have same phase. It includes two types.

- (a) **Gaseous phase catalysis :** When reactants and catalyst are in gaseous phase e.g. chamber process for  $\text{H}_2\text{SO}_4$ .



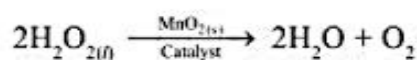
- (b) **Solution phase catalysis :** The reactions in which catalyst and reactants are in solution phase or liquid phase of miscible nature.



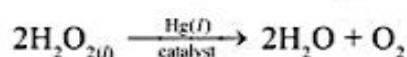


(ii) **Heterogeneous catalysis** : The reactions in which catalyst and reactants form phase  $\geq 2$ .

(a) **Solid-liquid catalysis** :  $\left. \begin{array}{l} \text{Reactant : Liquid} \\ \text{Catalyst : Solid} \end{array} \right\} \text{Immiscible}$



(b) **Liquid-Liquid catalysis** :  $\left. \begin{array}{l} \text{Reactant : Liquid} \\ \text{Catalyst : Liquid} \end{array} \right\} \text{Immiscible}$



(c) **Solid-gas catalysis** :  $\left. \begin{array}{l} \text{Reactant : gases} \\ \text{Catalyst : solid} \end{array} \right\} \text{Immiscible}$

Two aspects of solid catalyst are more significant, one is activity and the other is selectivity. Activity is the ability of catalyst to accelerate chemical reactions; the degree of acceleration can be as high as  $10^{10}$  times in certain reactions. Selectivity is the ability of catalyst to direct reaction to yield particular reaction (excluding others). For example, n-heptane selectivity gives toluene in presence of Pt catalyst. Similarly,

$\text{CH}_3-\text{CH}=\text{CH}_2 + \text{O}_2$  give  $\text{CH}_2=\text{CHCHO}$  selectivity over Bismuth molybdate catalyst.

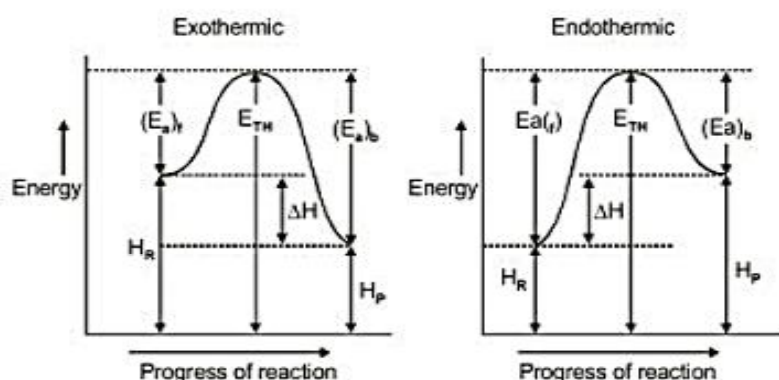
## 14. ARRHENIUS THEORY

### Threshold Energy and Activation Energy :

**Threshold energy** : For a reaction to take place the reacting molecules must collide together, but only those collisions, in which colliding molecules possess certain minimum energy is called threshold energy ( $E_T$ ) or the total minimum energy that reacting species must possess in order to undergo effective collision to form product molecules is called threshold energy.

**Activation energy** : It is extra energy which must be possessed by reactant molecules so that collision between reactant molecules is effective and leads to formation of product molecules.

$$E_a = E_{(\text{Threshold energy})} - E_{(\text{Reactant})}$$



$E_{TH}$  = Threshold Energy,  $H_R$  = Enthalpy or Energy or Potential of reactants.

$H_P$  = Enthalpy or Energy or Potential of product,  $(E_a)_f$  = Activation energy for forward reaction.

$(E_a)_b$  = Activation energy for backward reaction.



**Activated complex.** It is formed between reacting molecules which is highly unstable and readily changes into product.

$$\Delta H_{\text{react.}} = (E_a)_f - (E_a)_b$$

### Influence of Temperature on reaction rates

**Temperature coefficient :** The temperature coefficient of a chemical reaction is defined as the ratio of the reaction rates at two temperatures differing by  $10^\circ\text{C}$ . Its value usually lies between 2 & 3.

$$\text{Temperature coefficient} = \frac{k_{t+10}}{k_t}$$

If no temperature is specified in T.C. then it can be taken as  $25^\circ\text{C}$

**Arrhenius Equation :** A quantitative relationship was proposed by Arrhenius

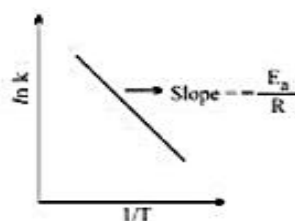
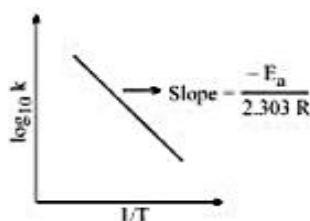
$$k = A \cdot e^{-E_a/RT}$$

where

$k$  = rate constant ;  $A$  = frequency factor (or pre-exponential factor);  
 $R$  = gas constant ;  $T$  = Temperature (kelvin);  $E_a$  = Activation energy.

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]$$

Graphical representations are :



### Illustration

1. In Arrhenius equation for a certain reaction, the value of  $A$  and  $E_a$  (activation energy) are  $4 \times 10^{13} \text{ sec}^{-1}$  and  $98.6 \text{ kJ mol}^{-1}$  respectively. At what temperature, the reaction will have specific rate constant  $1.1 \times 10^{-3} \text{ sec}^{-1}$ ?

**Sol.** According to Arrhenius equation

$$k = Ae^{-E_a/RT}$$

$$\text{or } \log_e k = \log_e A - \frac{E_a}{RT} \log_e e$$

$$2.303 \log_{10} k = 2.303 \log_{10} A - \frac{E_a}{RT}$$

$$\text{or } 2.303 \log (1.1 \times 10^{-3}) = 2.303 \log (4 \times 10^{13}) - \frac{98.6 \times 10^3}{8.314 \times T}$$

$$T = \frac{98.6 \times 10^3}{8.314 \times 2.303 \times 16.56} \text{ K} = 311 \text{ K}$$

2. The rate constant is given by Arrhenius equation

$$k = Ae^{-E_a/RT}$$

Calculate the ratio of the catalysed and uncatalysed rate constant at 25°C if the energy of activation of a catalysed reaction is 162 kJ and for the uncatalysed reaction the value is 350 kJ.

**Sol.** Let  $k_{ca}$  and  $k_{un}$  be the rate constants for catalysed and uncatalysed reactions.

$$2.303 \log_{10} k_{ca} = 2.303 \log_{10} A - \frac{162 \times 10^3}{RT} \quad \text{.....(i)}$$

$$\text{and } 2.303 \log_{10} k_{un} = 2.303 \log_{10} A - \frac{350 \times 10^3}{RT} \quad \text{.....(ii)}$$

Subtracting Eq. (ii) from Eq.(i)

$$\begin{aligned} \log_{10} \frac{k_{ca}}{k_{un}} &= \frac{10^3}{2.303RT} (350 - 162) \\ &= \frac{188 \times 10^3}{2.303 \times 8.314 \times 298} = 32.95 \end{aligned}$$

$$\frac{k_{ca}}{k_{un}} = 8.88 \times 10^{32}$$

3. At 407 K the rate constant of a chemical reaction is  $9.5 \times 10^{-5} \text{ s}^{-1}$  and at 420 K, the rate constant is  $1.9 \times 10^{-4} \text{ s}^{-1}$ . Calculate the frequency factor of the reaction.

**Sol.** The Arrhenius equation is,

$$\log_{10} \frac{k_2}{k_1} = \frac{E_a}{2.303 \times R} \left[ \frac{T_2 - T_1}{T_1 T_2} \right]$$

Given  $k_1 = 9.5 \times 10^{-5} \text{ s}^{-1}$ ;  $k_2 = 1.9 \times 10^{-4} \text{ s}^{-1}$ ;  
 $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ;  
 $T_1 = 407 \text{ K}$  and  $T_2 = 420 \text{ K}$

Substituting the values in Arrhenius equation.

$$\begin{aligned} \log_{10} \frac{1.9 \times 10^{-4}}{9.5 \times 10^{-5}} &= \frac{E_a}{2.303 \times 8.314} \left[ \frac{420 - 407}{420 \times 407} \right] \\ E_a &= 75782.3 \text{ J mol}^{-1} \end{aligned}$$

$$\text{Applying now } \log k_1 = \log A - \frac{E_a}{2.303 RT_1}$$

$$\log 9.5 \times 10^{-5} = \log A - \frac{75782.3}{2.303 \times 8.314 \times 407}$$

$$\begin{aligned} \text{or } \log \frac{A}{9.5 \times 10^{-5}} &= \frac{75782.3}{2.303 \times 8.314 \times 407} \\ &= 9.7246 \\ A &= 5.04 \times 10^5 \text{ s}^{-1} \end{aligned}$$

4. The energy of activation for a reaction is  $100 \text{ kJ mol}^{-1}$ . Presence of a catalyst lowers the energy of activation by 75%. What will be effect on rate of reaction at  $20^\circ\text{C}$ , other things being equal ?

Sol. The arrhenius equation is

$$k = Ae^{-E_a/RT}$$

In absence of catalyst,  $k_1 = Ae^{-100/RT}$

In presence of catalyst,  $k_2 = Ae^{-25/RT}$

$$\text{So } \frac{k_2}{k_1} = e^{75/RT} \quad \text{or } 2.303 \log \frac{k_2}{k_1} = \frac{75}{RT}$$

$$\text{or } 2.303 \log \frac{k_2}{k_1} = \frac{75}{8.314 \times 10^{-3} \times 293}$$

$$\text{or } \log \frac{k_2}{k_1} = \frac{75}{8.314 \times 10^{-3} \times 293 \times 2.303}$$

$$\text{or } \frac{k_2}{k_1} = 2.34 \times 10^{13}$$

As the things being equal in presence or absence of a catalyst,

$$\frac{k_2}{k_1} = \frac{\text{rate in presence of catalyst}}{\text{rate in absence of catalyst}}$$

$$\text{i.e., } \frac{r_2}{r_1} = \frac{k_2}{k_1} = 2.34 \times 10^{13}$$

### Exercise

The rate of a reaction triple when temperature changes from  $20^\circ\text{C}$  to  $50^\circ\text{C}$ . Calculate energy of activation for the reaction ( $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$ ).

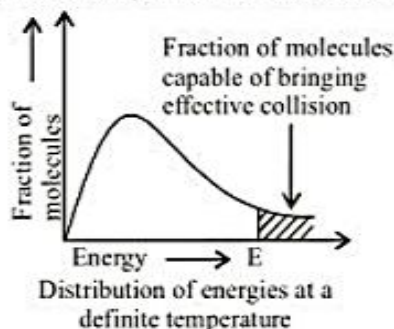
Ans.  $28.8118 \text{ kJ mol}^{-1}$

## 15. COLLISION THEORY

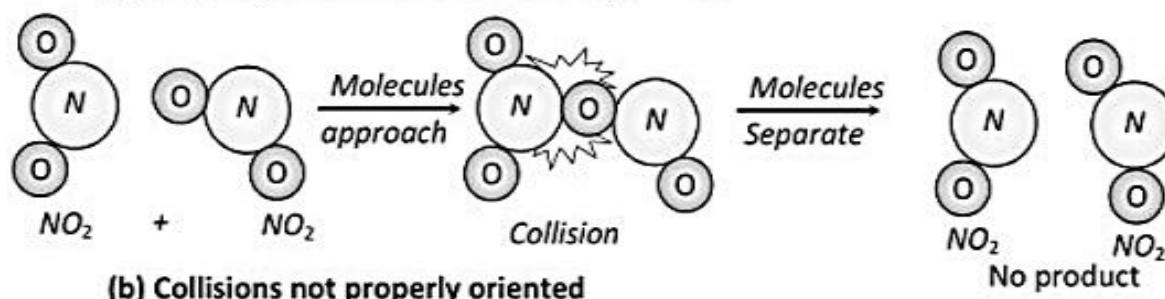
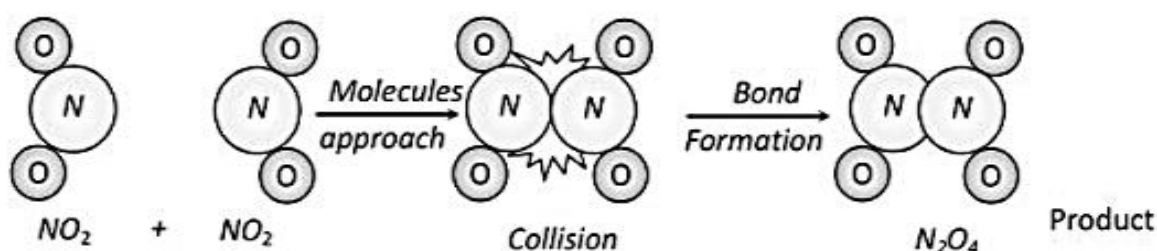
- The basic requirement for a reaction to occur is that the reacting species must collide with one another. This is the basis of **collision theory** for reactions.
- The number of collisions that takes place per second per unit volume of the reaction mixture is known as **collision frequency** ( $Z$ ).
- Every collision does not bring a chemical change. The collisions that actually produce the product are **effective collisions**. The effective collisions, which bring chemical change, are few in comparison to the total number of collisions. The collisions that do not form a product are **ineffective elastic collisions**, i.e., molecules just collide and disperse in different directions with different velocities.



- (iv) For a collision to be effective, the following two barriers are to be cleared.
- (a) **Energy barrier** : "The minimum amount of energy which the colliding molecules must possess as to make the chemical reaction to occur, is known as **threshold energy**".



- In the graph 'E' corresponds to minimum or threshold energy for effective collision.
  - There is an energy barrier for each reaction. The reacting species must be provided with sufficient energy to cross the energy barrier.
- (b) **Orientation barrier** : The colliding molecules should also have proper orientation so that the old bonds may break and new bonds are formed. For example,  $\text{NO}_2(\text{g}) + \text{NO}_2(\text{g}) \rightarrow \text{N}_2\text{O}_4(\text{g})$  During this reaction, the products are formed only when the colliding molecules have proper orientation at the time of collisions. These are called effective collisions.



- (v) Thus, the main points of collision theory are as follows,
- For a reaction to occur, there must be collisions between the reacting species.
  - Only a certain fraction of the total number of collisions is effective in forming the products.
  - For effective collisions, the molecules should possess sufficient energy as well as orientation.



- (vi) The fraction of effective collisions, under ordinary conditions may vary from nearly zero to about one for ordinary reactions. Thus, the rate of reaction is proportional to :
- The number of collisions per unit volume per second (Collision frequency,  $Z$ ) between the reacting species
  - The fraction of effective collisions (Properly oriented and possessing sufficient energy),  $f$

i.e.,  $\text{Rate} = \frac{-dx}{dt} = f \times Z$ ; Where  $f$  is fraction of effective collision and  $Z$  is the collision frequency.

- (vii) The physical meaning of the activation energy is that it is the minimum relative kinetic energy which the reactant molecules must possess for changing into the products molecules during their collision.

This means that the fraction of successful collision is equal to  $e^{-E_a/RT}$  called **Boltzmann factor**.

- (viii) It may be noted that besides the requirement of sufficient energy, the molecules must be properly oriented in space also for a collision to be successful. Thus, if  $Z_{AB}$  is the collision frequency,  $P$  is the **orientation factor** (Steric factor) then,  $k = PZ_{AB} \cdot e^{-E_a/RT}$ . If we compare this equation with Arrhenius equation  $k = Ae^{-E_a/RT}$ .

We know that pre-exponential form 'A' in Arrhenius equation is,  $A = PZ_{AB}$ .

## SOLVED EXAMPLE

**Q.1** In the following reaction  $2\text{H}_2\text{O}_2 \longrightarrow 2\text{H}_2\text{O} + \text{O}_2$   
rate of formation of  $\text{O}_2$  is  $3.6 \text{ M min}^{-1}$ .

(a) What is rate of formation of  $\text{H}_2\text{O}$ ?

(b) What is rate of disappearance of  $\text{H}_2\text{O}_2$ ?

**Ans.** (i)  $7.2 \text{ mol litre}^{-1} \text{ min}^{-1}$ , (ii)  $7.2 \text{ mol litre}^{-1} \text{ min}^{-1}$

**Sol.** 
$$\frac{d}{dt} [\text{H}_2\text{O}_2] = \frac{d}{dt} [\text{H}_2\text{O}] = 2 \times \frac{d}{dt} [\text{O}_2]$$

**Q.2** In a catalytic experiment involving the Haber process,  $\text{N}_2 + 3\text{H}_2 \longrightarrow 2\text{NH}_3$ , the rate of formation of Ammonia was measured as

$$\text{Rate} = \frac{\Delta[\text{NH}_3]}{\Delta t} = 2 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}.$$

If there were no side reactions, what was the expressed in terms of (a)  $\text{N}_2$ , (b)  $\text{H}_2$ ?

**Ans.** (a)  $1 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$ , (b)  $3 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$

**Sol.** (a) 
$$\frac{d[\text{N}_2]}{dt} = \frac{1}{3} \frac{d[\text{H}_2]}{dt} = \frac{1}{2} \frac{d[\text{NH}_3]}{dt}$$

$$\therefore r = \frac{d}{dt} [\text{N}_2] = \frac{1}{2} \times (2 \times 10^{-4}) = 10^{-4}$$

(b) 
$$\frac{d}{dt} [\text{H}_2] = \frac{3}{2} \times (2 \times 10^{-4}) = 3 \times 10^{-4}$$

**Q.3** For the elementary reaction  $2\text{A} + \text{B}_2 \longrightarrow 2\text{AB}$ . Calculate how much the rate of reaction will change if the volume of the vessel is reduced to one third of its original volume?

**Ans.** rate increase by 27 times

**Sol.**  $\text{Rate} = K [3\text{A}]^2 [3\text{B}_2] = 27 \text{ Rate}.$

**Q.4** In the following reaction, rate constant is  $1.2 \times 10^{-2} \text{ M s}^{-1}$   $\text{A} \longrightarrow \text{B}$ . What is concentration of B after 10 and 20 min., if we start with 10 M of A.

**Ans.** (i) 7.2 M, (ii) Think

**Sol.** (a)  $K = \frac{1}{t} [A_0 - A] \Rightarrow Kt = [B]$   
 $\Rightarrow 1.2 \times 10^{-2} \times 10 \times 60 = [B] = 7.2$

(b) Same way

**Q.5** A first order reaction is 75% completed in 72 min.. How long time will it take for

(i) 50% completion

(ii) 87.5% completion

**Ans.** (i) 36 min., (ii) 108 min.

Sol.  $K = \frac{2.303}{72} \log_{10} \frac{100}{25} = 0.19$

(i)  $t_{1/2} = \frac{0.693}{.019} = 36$

(ii)  $t = \frac{2.303}{.019} \log_{10} \frac{100}{12.5} = 108$

**Q.6** Show that in case of unimolecular reaction, the time required for 99.9% of the reaction to take place is ten times that required for half of the reaction.

Sol.  $\frac{t_1}{t_2} = \frac{3}{0.3}$  Calculate  $t_1$  &  $t_2$  separately  
 $\therefore t_1 = 10 t_2$

**Q.7** The half life of the unimolecular elementary reaction  $A(g) \longrightarrow B(g) + C(g)$  is 6.93 min. How long will it take for the concentration of A to be reduced to 10 % of the initial value?

(A) 10.053 min (B) 4.6 min (C) 46 min (D) 23.03 min

**Ans.** (D)

Sol.  $\frac{0.693}{6.93} \times t = 2.303 \log \frac{[A]_0}{0.1[A]_0} \Rightarrow t = 23.03 \text{ min}$

**Q.8** A 1 L reaction vessel which is equipped with a movable piston is filled completely with a 1 M aqueous solution of  $H_2O_2$ . The  $H_2O_2$  decomposes to  $H_2O(l)$  and  $O_2(g)$  in a first order process with half life 5 hrs at 300 K. As gas formed, the piston moves up against constant external pressure of 1 atm. What is the net work done by the gas from the start of sixth hour till the end of 10 hrs?

(A) 25 Cal (B) 150 Cal (C) 75 Cal (D) 100 Cal

**Ans.** (C)

**Sol.** At the end of 5 hours

$$A_{t,1} = \frac{A_0}{2}$$

at the end of 10<sup>th</sup> hours

$$A_{t,2} = \frac{A_0}{4}$$

$$A_{t,2} - A_{t,1} = \frac{A_0}{2} - \frac{A_0}{4} = \frac{A_0}{4} = 0.25 A_0$$

amount decayed = 0.25 mol

moles of  $O_2$  formed =  $0.25/2 = 1/8$

$$W = -P\Delta V = -nRT = -(1/8) \times 300 \times 2 \text{ Cal} = 75 \text{ Cal}$$

**Q.9** At a certain temperature the following data were collected for the reaction



Initial Concentrations (M)		Initial Rate of formation of $\text{I}_2$ ( $\text{Ms}^{-1}$ )
[ICl]	[ $\text{H}_2$ ]	
0.10	0.10	0.0015
0.20	0.10	0.0030
0.10	0.05	0.00075

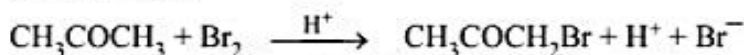
Determine overall order of reaction

- (A) 0 (B) 1 (C) 2 (D) 3

**Ans.** (C)

**Sol.** From 1<sup>st</sup> and 2<sup>nd</sup> data order of reaction w.r.t. ICl is 1, from 1<sup>st</sup> and 3<sup>rd</sup> data order of reaction w.r.t.  $\text{H}_2$  is 1, so overall order of reaction is 2.

**Q.10** For the reaction



the following data was collected

[Acetone]	[ $\text{Br}_2$ ]	[ $\text{H}^+$ ]	Rate of reaction ( $\text{Ms}^{-1}$ )
0.15	0.025	0.025	$6 \times 10^{-4}$
0.15	0.050	0.025	$6 \times 10^{-4}$
0.15	0.025	0.050	$12 \times 10^{-4}$
0.20	0.025	0.025	$8.0 \times 10^{-4}$

The order of the reaction w.r.t.  $\text{CH}_3\text{COCH}_3$  and  $\text{Br}_2$  respectively are :

- (A) 0,1 (B) 1,0 (C) 1,1 (D) 1,2

**Ans.** (B)

**Sol.** Rate =  $k \cdot [\text{Acetone}]^x \cdot [\text{Br}_2]^y \cdot [\text{H}]^z$

$$6 \times 10^{-4} = k \cdot (0.15)^x (0.025)^y (0.025)^z \quad \dots (i)$$

$$6 \times 10^{-4} = k \cdot (0.15)^x (0.050)^y (0.025)^z \quad \dots (ii)$$

$$12 \times 10^{-4} = k \cdot (0.15)^x (0.025)^y (0.050)^z \quad \dots (iii)$$

$$8 \times 10^{-4} = k \cdot (0.20)^x (0.025)^y (0.025)^z \quad \dots (iv)$$

$$(i) \div (ii), 1 = \left( \frac{0.025}{0.050} \right)^y$$

$y = 0$ , hence rate does not depend upon the concentration of  $\text{Br}_2$ .

$$(i) \div (iii), \frac{6}{12} = \left( \frac{0.025}{0.050} \right)^z ; \frac{1}{2} = \left( \frac{1}{2} \right)^z$$

$$\therefore z = 1$$

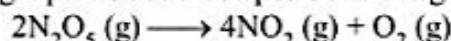
$$(i) \div (iv), \frac{3}{4} = \left( \frac{3}{4} \right)^x$$

$$\therefore x = 1$$



**Direction for Q.11 and Q.12 (2 questions) :** Read the following passage carefully and answer the questions given after the passage.

Dinitrogen pentoxide decomposes on heating to nitrogen dioxide and oxygen following first order kinetics.



0.2 mole of  $\text{N}_2\text{O}_5$  was taken in a vessel of capacity 1 L and heating to a certain temperature of T Kelvin at which the reaction begins. The concentration of  $\text{N}_2\text{O}_5$  is measured at different intervals of time by withdrawing samples of reaction mixture. A plot of  $\ln[\text{N}_2\text{O}_5]$  v/s time is shown in figure-1. The value of rate constant (k) of the reaction is determined from the slope of the linear plot. The same experiment is repeated at five different temperatures and the value of the rate constants are calculated at each temperature. A plot of  $\ln k$  v/s  $(\text{temperature})^{-1}$  is shown in figure-2.

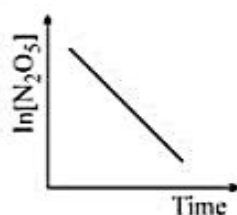


Fig-1

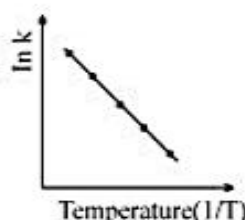


Fig-2

- Q.11** Slope of straight line in figure-2 is  $-1.2 \times 10^4 \text{ K}$ . What is the activation energy of the reaction? (J/mole)  
 (A)  $1.0 \times 10^5 \text{ J mole}^{-1}$  (B)  $2.303 \times 10^5 \text{ mole}^{-1}$  (C)  $1.2 \times 10^5 \text{ mole}^{-1}$  (D)  $2.5 \times 10^5 \text{ mole}^{-1}$

**Ans.** (A)

**Sol.**  $\ln k = \frac{-E_a}{RT} + \ln A$

$$\text{slope} = \frac{-E_a}{R} = -1.2 \times 10^4$$

$$E_a = 1.2 \times 10^4 \times 8.314 = 9.97 \times 10^4 \text{ Joule}$$

- Q.12** Slope of straight line in figure-1 is  $-1 \times 10^{-1} \text{ sec}^{-1}$ . What is the half-life of the reaction?  
 (A) 15.96 sec (B) 6.93 sec (C) 693 sec (D) 31.92 sec

**Ans.** (B)

**Sol.**  $Kt = \ln A_0 - \ln A_t$   
 $\ln A_t = \ln A_0 - Kt$   
 $\text{slope} = -K = -(1 \times 10^{-1})$

$$t \frac{1}{2} = \frac{0.693}{10^{-1}} = 6.93 \text{ sec}$$

- Q.13** The rate constant for an isomerisation reaction  $A \rightarrow B$  is  $4.5 \times 10^{-3} \text{ min}^{-1}$ . If the initial concentration of A is 1 M. Calculate the rate of the reaction after 1 h.

**Ans.**  $3.435 \times 10^{-3} \text{ M/min}$

**Sol.**  $k = \frac{2.303}{t} \log \frac{a}{a-x}$

$$4.5 \times 10^{-3} = \frac{2.303}{60} \log \frac{1}{(a-x)} \Rightarrow (a-x) = 0.7633$$

$$\begin{aligned} \text{Rate} &= k[a-x] \\ &= 4.5 \times 10^{-3} \times 0.7633 = 3.43 \times 10^{-3} \end{aligned}$$

- Q.14** A hydrogenation reaction is carried out at 500 K. If the same reaction is carried out in the presence of a catalyst at the same rate, the temperature required is 400 K. Calculate the activation energy of the reaction if the catalyst lowers the activation barrier by 20 kJmol<sup>-1</sup>.

**Ans.** 100 kJmol<sup>-1</sup>

**Sol.**  $k = Ae^{-E_a/RT} = Ae^{-E_a'/RT}$   
Given that two rate are same

$$e^{-E_a/RT} = e^{-E_a'/RT'}$$

$$\frac{E_a}{T} = \frac{E_a - 20}{T'}$$

$$\frac{E_a}{500} = \frac{E_a - 20}{400} \text{ or } E_a = 100 \text{ kJ}$$

- Q.15** The energy of activation of a first order reaction is 104.5 kJ mole<sup>-1</sup> and pre-exponential factor (A) is  $5 \times 10^{13} \text{ sec}^{-1}$ . At what temperature, will the reaction have a half life of 1 minute?

**Ans.** 349.1 k

**Sol.**  $k = A \cdot e^{-E_a/RT}$

$$\log k = \log A - \frac{E_a}{RT}$$

$$\log \frac{0.693}{t_{1/2}} = \log A - \frac{E_a}{2.303RT}$$

$$\log \frac{0.693}{60} = \log 5 \times 10^{13} - \frac{104.5}{2.303 \times 8.314 \times 10^{-3} \times T}$$

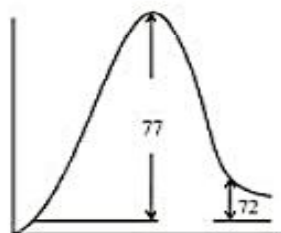
$$-1.9412 = 13.699 - \frac{104.5}{0.019147T}$$

$$T = 348.95$$

- Q.16** In gaseous reactions important for understanding the upper atmosphere, H<sub>2</sub>O and O react bimolecularly to form two OH radicals.  $\Delta H$  for this reaction is 72 kJ at 500 K and  $E_a = 77 \text{ kJ mol}^{-1}$ , then calculate  $E_a$  for the biomolecular recombination of 2OH radicals to form H<sub>2</sub>O & O at 500 K

**Ans.** 5 kJ mol<sup>-1</sup>

**Sol.**



$$E_{a,b} = 77 - 72 = 5$$

# ALCOHOL

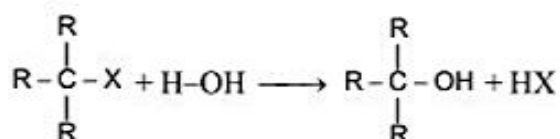
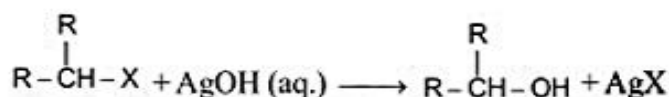
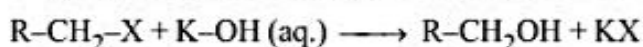
## INTRODUCTION

- (a) These are the organic compounds in which -OH group is directly attached with carbon.
- (b) These are hydroxy derivatives of alkanes and mono alkyl derivatives of water.
- (c) Their general formula is  $C_nH_{2n+1}OH$  or  $C_nH_{2n+2}O$ .
- (d) The hybridisation state of carbon is  $sp^3$ .
- (e) Geometry is tetrahedral.
- (f) In these compounds C-O bond length is 1.42 Å.
- (g) These are of following types, depending upon the no. of OH groups.
  - (i) Monohydric alcohol : Contains one -OH group only, eg.  $C_2H_5OH$
  - (ii) Dihydric alcohol : Contains two -OH groups. eg. glycol
  - (iii) Trihydric alcohol : Contains three -OH groups eg. glycerol
  - (iv) Polyhydric alcohol : Contains more than three -OH groups. eg. sorbitol, manitol.
- (h) Alcohol shows chain, position & functional group isomerism. If chiral carbon atom is present, they shows optical isomerism.

## METHODS OF PREPARATION

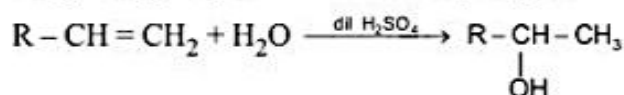
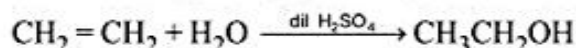
### From Alkyl halides :

Alkyl halides reacts with aq. KOH/aq. AgOH or  $H_2O$  and forms alcohol.



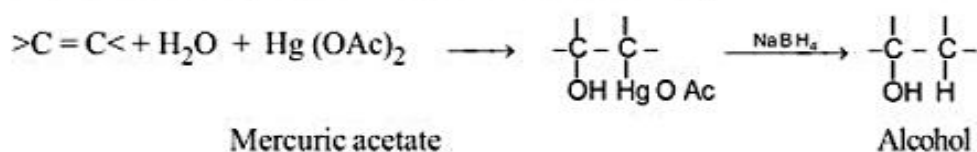
### From Alkenes :

**Hydration** – Alkenes are catalytically hydrated by dilute mineral acid solution.



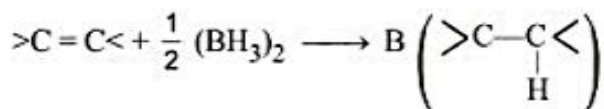
### Oxymercuration – demercuration :

Alkenes react with mercuric acetate in the presence of water to give hydroxymercurial compounds, which on reduction yield alcohols. (Markovnikov addition)

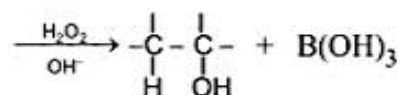
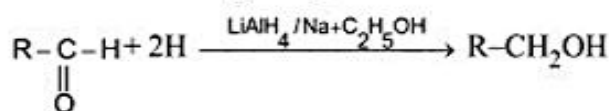


**Hydroboration – Oxidation :**

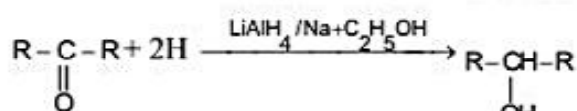
(Anti-Markownikov orientation)



Alkene      Diborane                  Tri alkyl borane

**By Reduction of Carbonyl compounds :-**

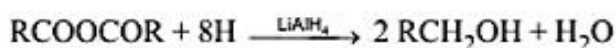
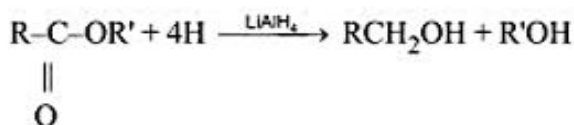
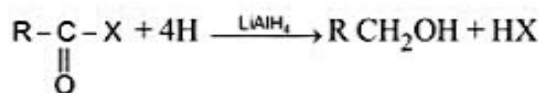
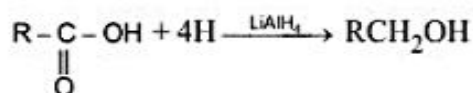
1° alcohol



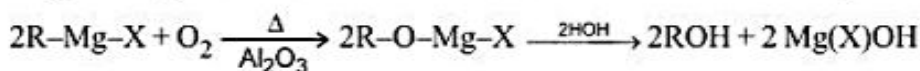
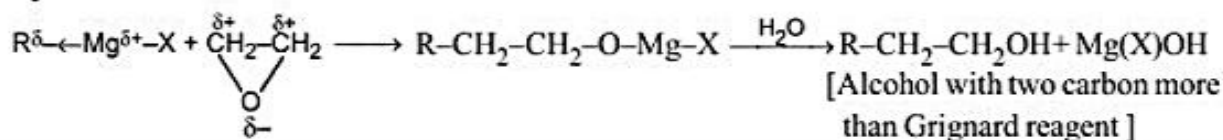
2° alcohol

**Note :**

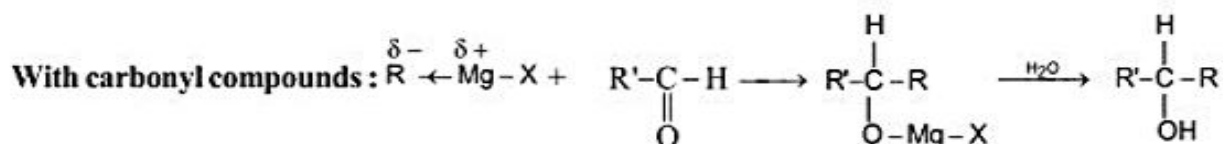
- (i) We cannot obtain 3° alcohol from this method
- (ii) If we use NaH as reductant then the process is called as 'Darzen's process'.

**By Reduction of Acid & its derivatives :****Important Note :-** Acid amide does not form alcohol on reduction. It forms primary amine.**From Grignard reagent :****With oxygen :-**

Grignard reagent forms alcohol of same no. of carbon atoms as in Grignard reagent.

**With ethylene oxide :**

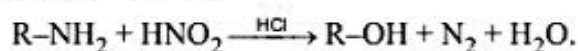




**Note :**

- (i) If  $R' = H$ , Product will be 1° alcohol.
- (ii) If  $R' = R$ , Product will be 2° alcohol.
- (iii) If carbonyl compound is ketone, product will be 3° alcohol.
- (iv) It is the best method for preparation of alcohol because we can prepare every type of alcohols.

**From Primary amines :-**



But it is not a good method for preparation of alcohol because a number of by products are formed in this reaction like alkyl chloride, alkyl nitrite, alkene and ether.

**Note :** In this reaction if we take ethyl amine then main product will be ethanol while if we take methyl amine, then main product will be dimethyl ether.

## PHYSICAL PROPERTIES

- (a) Alcohols are colourless with specific smell liquid. They are soluble in water due to H-bonding. These are partially soluble in organic solvents.
- (b) They are liquid in nature up to 12-carbon.
- (c) Melting point and Boiling point  $\propto$  molecular mass  $\propto \frac{1}{\text{No. of branches}}$
- (d) Boiling point of alcohols are higher than equivalent ethers. It is due to H-bonding.
- (e) Alcohols are poisonous in nature also. Poisonous character increase with increment in molecular weight or branching. Ethanol is exception, which is non-poisonous in nature. It is most useful organic solvent.
- (f) Methanol causes blindness.
- (g) Isopropyl alcohol is called as rubbing alcohol.
- (h) Cholesterol is also an example of complex alcohol which is called notorious alcohol because it causes heart attack.
- (i) Viscous nature of alcohol is directly proportional to H-bonding or number of -OH groups. That is why we can say alcohol is less viscous than glycerol & manitol is more viscous than glycerol.
- (j) Ethanol is liquid while glucose is solid. It is due to more H-bonding in glucose.

## CHEMICAL PROPERTIES

Chemical reactions of alcohols are classified in the following three types :-

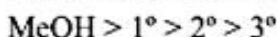
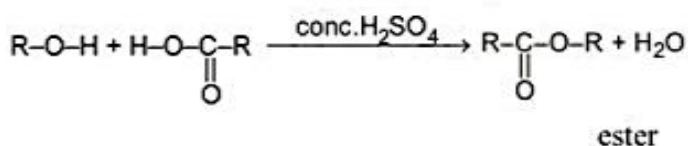
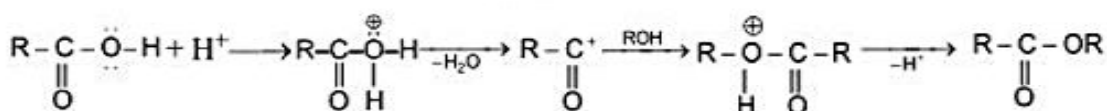
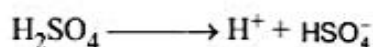
- (i) Reaction of H atom of -OH group of Alcohols
- (ii) Reaction of OH group of Alcohols
- (iii) General reaction of Alcohols.

**Reaction of H atom of -OH group of Alcohols :**

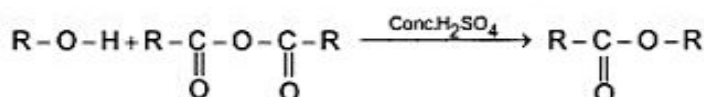
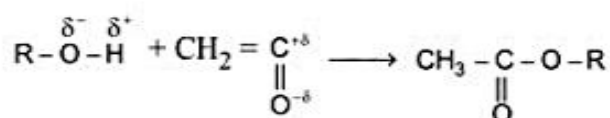
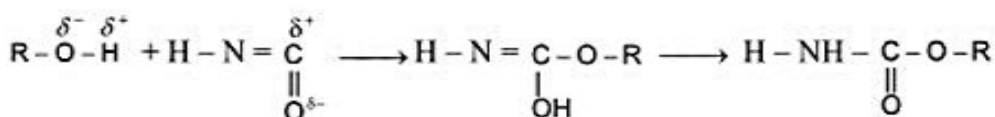
These are the reactions in which alcohol shows acidic character.

**Reaction with Na :**

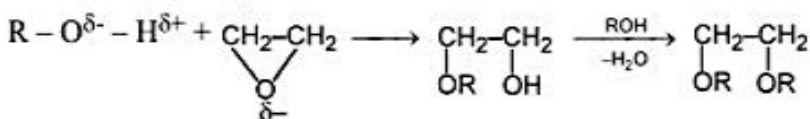
The acidic order of alcohols is

**Esterification / Reaction with carboxylic acid:-****Mechanism :**

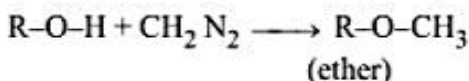
**Note :** The above reaction is laboratory method of ester preparation.

**Reaction with Acid derivatives :****Reaction with Ketene :-****Reaction with Isocyanic Acid :-**

amino ester (urethane)

**Reaction with ethylene oxide :**

1,2-dialkoxy ethane

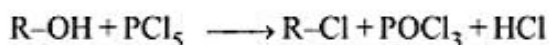
**Reaction with Diazomethane :-**

## Reaction of –OH group of Alcohols :-

### Reaction with dry HX (Grove's Process) :



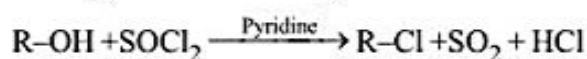
### Reaction with $PCl_5$ :



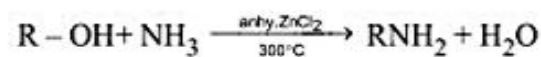
### Reaction with $PCl_3$ :



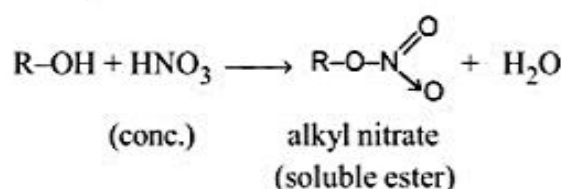
### Reaction with $SOCl_2$ (Darzen reaction) :



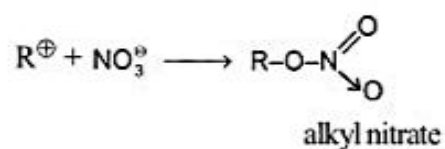
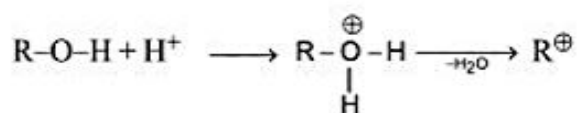
### Reaction with ammonia :



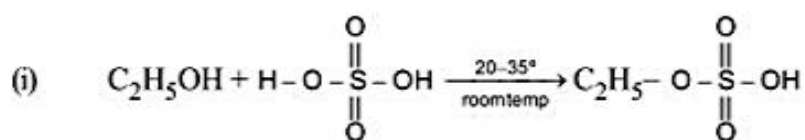
### Reaction with $HNO_3$ :



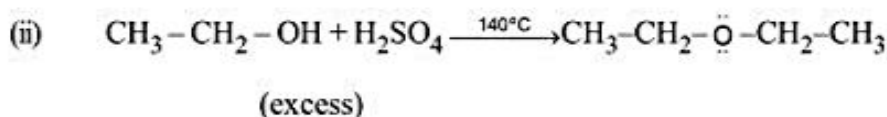
### Mechanism :-

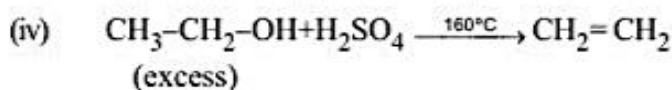
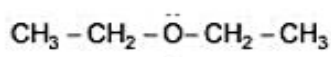
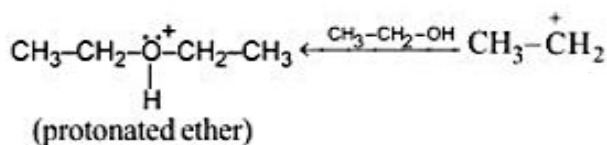
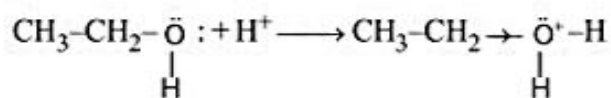
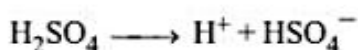
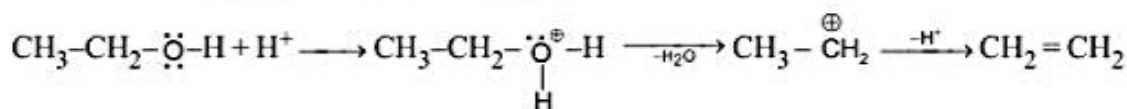
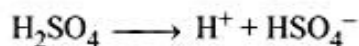


### Reaction with $H_2SO_4$ :-

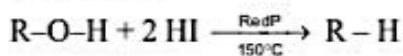


stable upto (80-100°C)

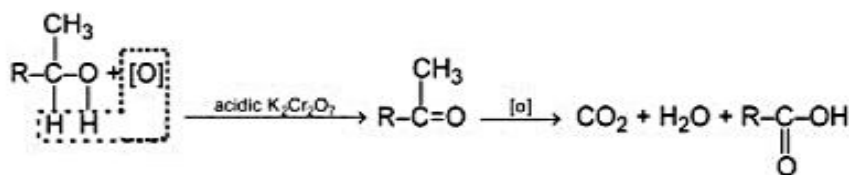
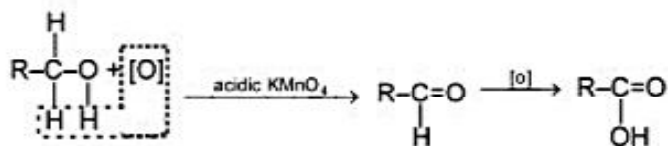


**Mechanism :-****Mechanism :-**

**Note :** In the above reaction excess of ethanol is present so, intermediate carbocation satisfies itself by elimination.

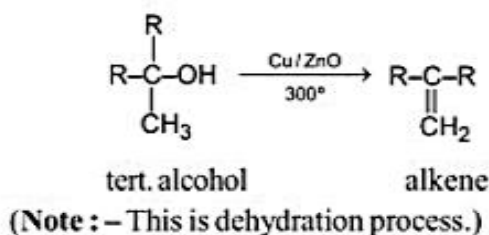
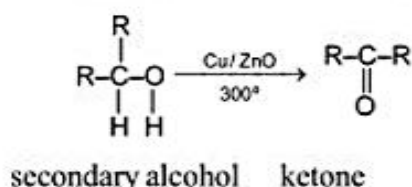
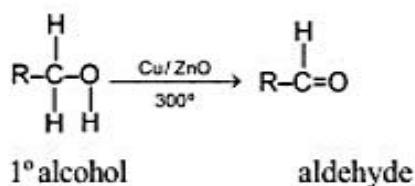
**GENERAL REACTION OF ALCOHOLS****Reduction :-**

Reacting species of solution is  $\text{HCrO}_4^-$ .



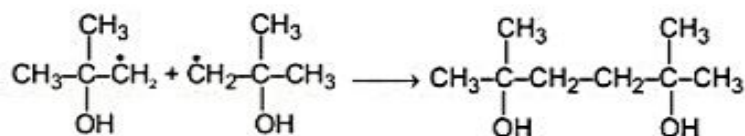
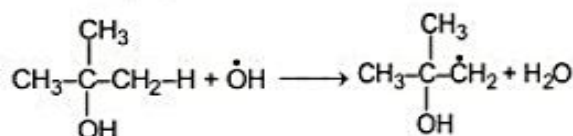
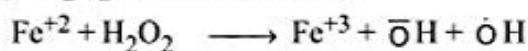


### Catalytic Oxidation / Dehydrogenation :



### Oxidation through Fenton's Reagent :

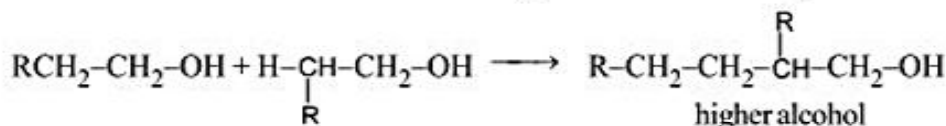
Higher and branched alcohols are converted into diols through Fentons reagent. ( $\text{FeSO}_4 + \text{H}_2\text{O}_2$ ) is Fenton's reagent.



2,5-dimethyl hexandiol-2,5

### Self Condensation :

When alcohol is heated with sodium ethoxide then by self condensation they convert into higher alcohol.

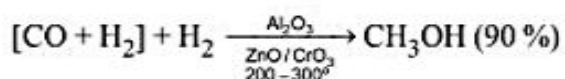


Note : The above reaction is called as 'Guerbet's Reaction'.

### Preparation of methanol :

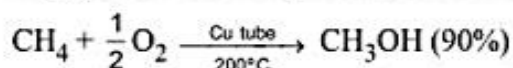
Methanol is also called as carbinol or wood spirit.

#### From Water Gas :



**From Methane :-**

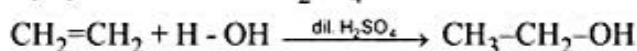
$\text{CH}_4$  gives methanol on partial oxidation in Cu tube.



### Preparation of Ethanol :

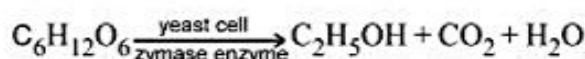
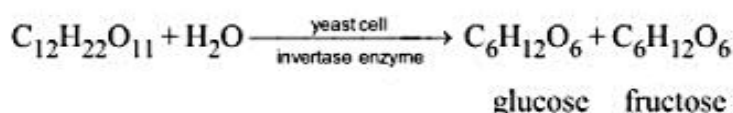
**From Ethene :**

By hydration with dil.  $H_2SO_4$



**Preparation of ethanol from sugar : -**

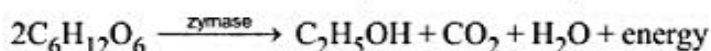
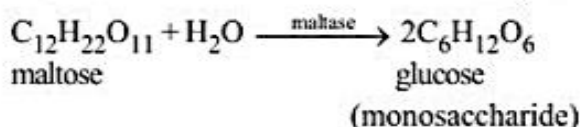
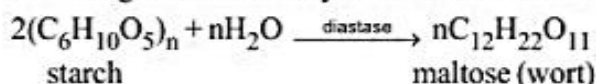
- (i) **Molasses :** - Waste product in sugar industry is called molasses. It is a mixture of sugar (30%) and invert sugar (32-40%).
- (ii) **Invert sugar :** - Combine form of glucose and fructose is called as invert sugar.



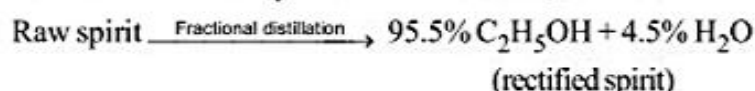
**Note:** Glucose and fructose are functional isomers.

### Preparation of ethanol from starch :

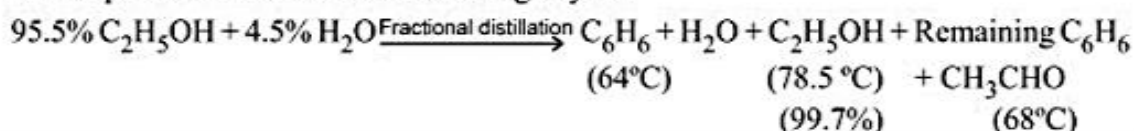
- (i) Starch solution is technically called 'Mesh'
- (ii) Crushed germinated barley solution is called 'Malt'.

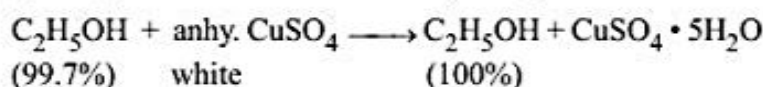
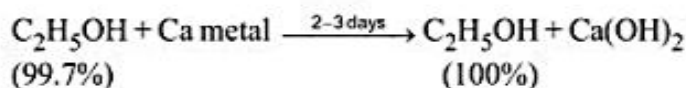


- (iii) From both of the methods conc. of ethanol achieved is 10-12% which is called 'Wash'.
- (iv) Distillation of wash is done in special apparatus 'Coffee's still', which is based on counter current method. From this distillation yield of alcohol is 90%, which is called Raw spirit.



- (v) Further purification is done in the following ways :-





## DIFFERENCE BETWEEN PRIMARY, SECONDARY & TERTIARY ALCOHOLS

**By Oxidation Reaction :** Primary alcohol gives aldehyde on oxidation, secondary alcohol gives ketone and tertiary alcohols are resistant to oxidation.

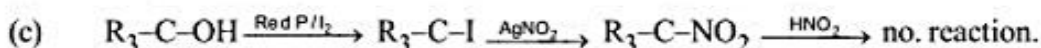
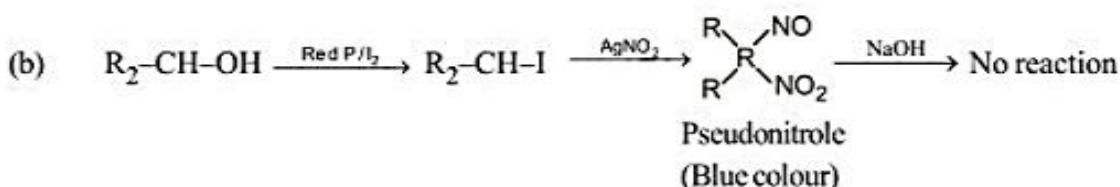
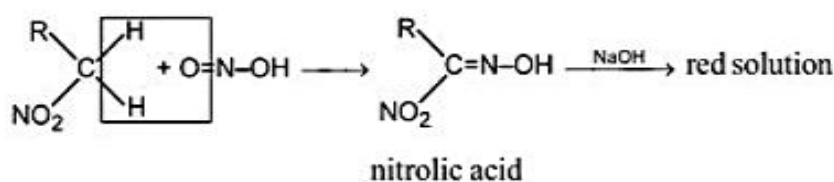
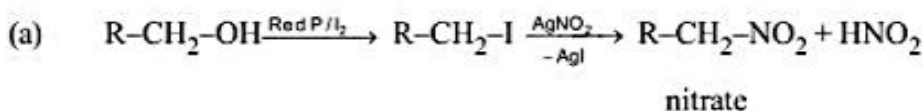
**By Catalytical Oxidation / Dehydrogenation :** Primary alcohol gives aldehyde on oxidation, secondary alcohol gives ketone and tertiary alcohol gives alkene (dehydration takes place in this condition to tertiary alcohols.)

**Lucas Test :** A mixture of (anhydrous  $\text{ZnCl}_2$  + Conc.  $\text{H}_2\text{SO}_4$ ) is called as **Lucas Reagent**.

- (i) 3° alcohol gives white ppt. with lucas reagent in 2-3 seconds only.
- (ii) 2° alcohol takes 9 - 10 minutes.
- (iii) 1° alcohol does not give white ppt. at room temperature.

**Victor Meyer Test : -**

This test is also known as RBW ( Red, Blue, White) test.



### Difference between Methanol and Ethanol

Methanol	Ethanol
1. When $\text{CH}_3\text{OH}$ is heated on Cu coil it gives formalin like smell.	Ethanol does not give formalin like smell.
2. When $\text{CH}_3\text{OH}$ is heated with salicylic acid in $\text{H}_2\text{SO}_4$ (conc.) then methyl salicylate is formed which has odour like winter green oil	No such odour is given by ethanol
3. It does not give haloform or Iodoform test.	It gives haloform test.

### MCQ

- Q.1** Which of the following reaction is called as 'Bouveault-Blanc reduction' -  
 (A) Reduction of acyl halide through  $\text{Na}/\text{C}_2\text{H}_5\text{OH}$   
 (B) Reduction of ester through  $\text{Na}/\text{C}_2\text{H}_5\text{OH}$   
 (C) Reduction of anhydride through  $\text{Na}/\text{C}_2\text{H}_5\text{OH}$   
 (D) Reduction of carbonyl compounds through  $\text{Na}/\text{C}_2\text{H}_5\text{OH}$
- Q.2** In which of the following reaction alcohol is not formed-  
 (A)  $\text{R}-\text{CH}=\text{CH}_2 + \text{H}_2\text{O} \xrightarrow[\text{High pr.}]{\text{H}^+}$  (B)  $\text{R}-\text{COCl} + 2\text{H}_2 \xrightarrow{\text{LiAlH}_4}$   
 (C)  $(\text{R}-\text{CO})_2\text{O} + 4\text{H}_2 \xrightarrow{\text{LiAlH}_4}$  (D)  $\text{R}-\text{CH}_2-\text{CH}_3 + \text{H}_2\text{O} \xrightarrow[\text{High pr.}]{\text{H}^+}$
- Q.3** Which one of the following alcohol has highest boiling point -  
 (A) Methanol (B) Ethanol (C) Propanol (D) Isopropanol
- Q.4** Dimethyl ether and ethanol have same molecular weight but boiling point of ethanol is greater than dimethyl ether, cause of this is that dimethyl ether -  
 (A) Having less no. of branches  
 (B) Arrangement of hydrogen is different  
 (C) Due to hydrogen bonding in alcohol  
 (D) None of these
- Q.5** Reactivity order of alcohols towards Na will be -  
 (A)  $3^\circ > 2^\circ > 1^\circ > \text{MeOH}$  (B)  $\text{MeOH} > 1^\circ > 2^\circ > 3^\circ$   
 (C)  $2^\circ > 1^\circ > 3^\circ > \text{MeOH}$  (D)  $1^\circ = 2^\circ = 3^\circ = \text{MeOH}$
- Q.6** In the esterification of alcohol by carboxylic acid, proton is given by -  
 (A) Alcohol (B) Conc.  $\text{H}_2\text{SO}_4$  (C) Acid carboxylic (D) None of these



- Q.7** 2-methyl 2-propanol with Fenton's reagent gives -  
 (A) 1,2-methyl propene -1 (B) 2-methyl propene -2  
 (C) 2,5-dimethyl hexanediol-2,5 (D) 2,2,3,3 - tetramethyl butane
- Q.8** When methane is passed in copper tube at 200°C with air, it gives -  
 (A) Methanol (B) Ethanol (C) Acetylene (D) Ethene
- Q.9** Acetic acid is removed from pyroligneous acid by the passing it in -  
 (A) Al (OH)<sub>3</sub> solution (B) Ba (OH)<sub>2</sub> solution  
 (C) Ca (OH)<sub>2</sub> solution (D) Ethanol
- Q.10** Crushed germinated barley solution is called-  
 (A) Mesh (B) Malt (C) Wort (D) Wash
- Q.11** Which one test is also known as RBW test-  
 (A) Lucas test (B) Victor Meyer test  
 (C) Carbilamine test (D) Mullican-Barker test

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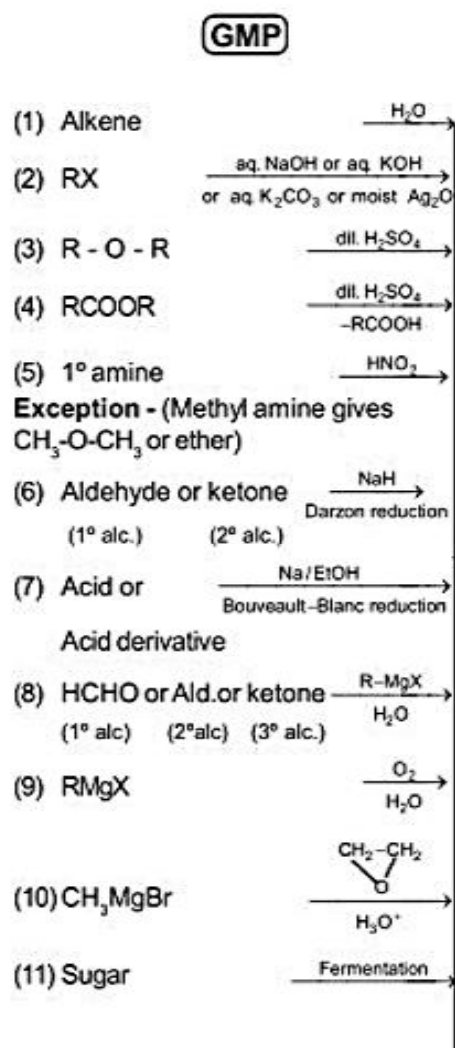
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#### ANSWER KEY

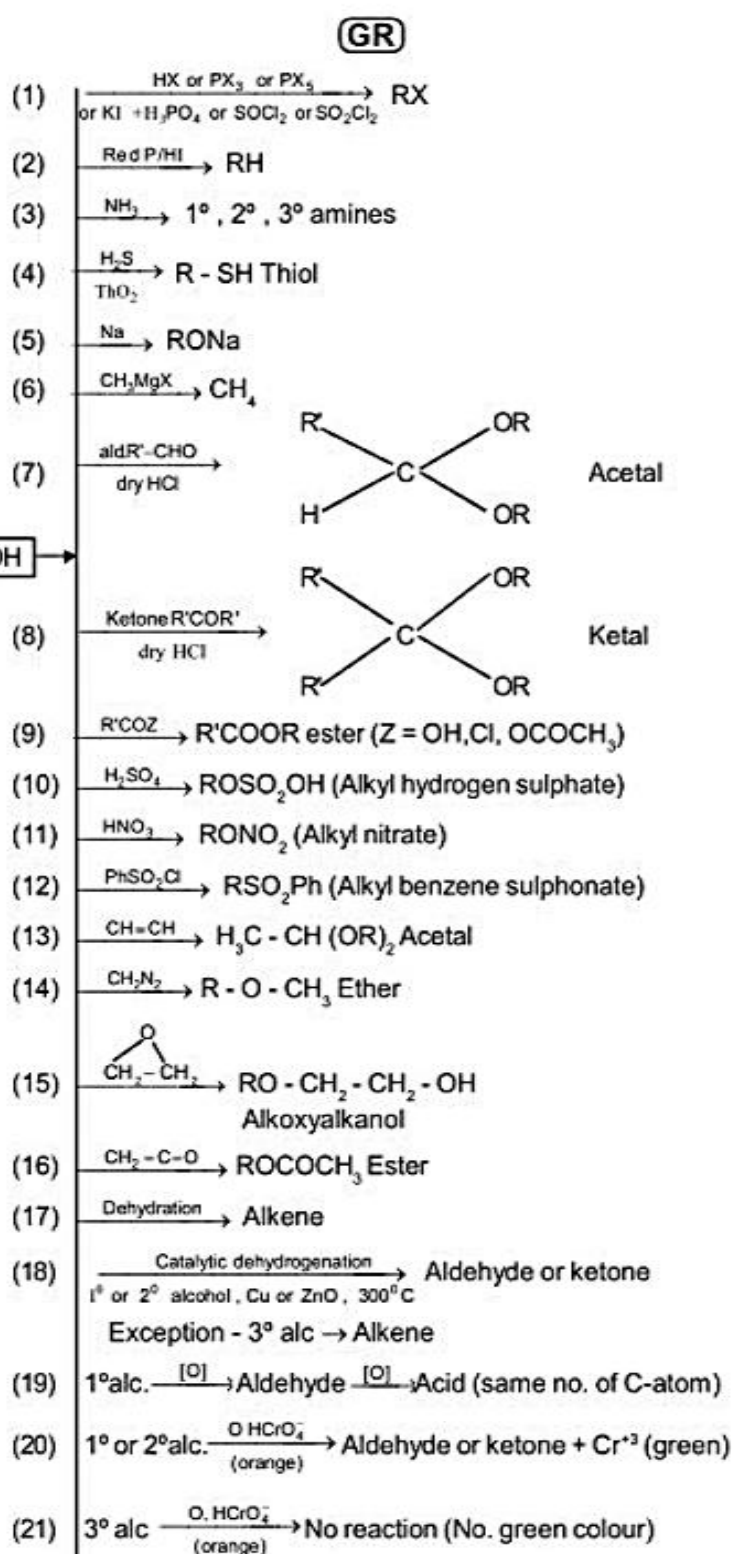
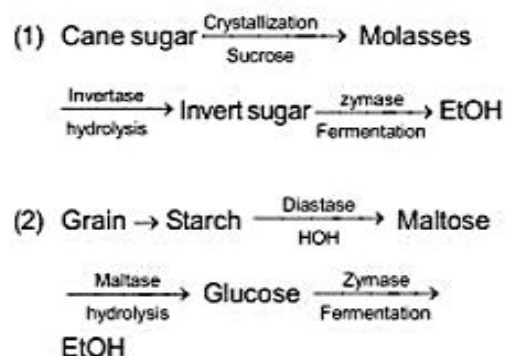
<b>Q.1</b>	(D)	<b>Q.2</b>	(D)	<b>Q.3</b>	(C)	<b>Q.4</b>	(C)	<b>Q.5</b>	(B)	<b>Q.6</b>	(B)
<b>Q.7</b>	(C)	<b>Q.8</b>	(A)	<b>Q.9</b>	(C)	<b>Q.10</b>	(B)	<b>Q.11</b>	(B)		

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# ALCOHOL



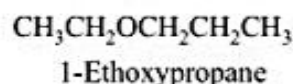
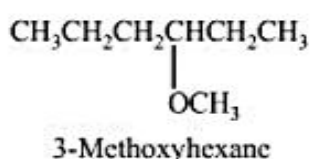
## Formation of EtOH by fermentation -



## ETHERS

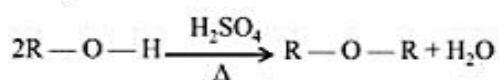
### INTRODUCTION

- (a) It is dialkyl derivative of water or alkoxy derivative of alkane or monoalkyl derivative of alcohols.
- (b) Their general formula is  $C_nH_{2n+2}O$  or  $C_nH_{2n+1}O$
- (c) Hybridisation state of oxygen is  $sp^3$  and bond angle is  $110^\circ$  due to counter balance repulsion of alkyl groups.
- (d) If both alkyl groups are similar then these are called as simple ether, if different they are called as mixed ether.
- (e) Carbon oxygen bond length is  $1.42 \text{ \AA}$ .
- (f) Ether shows chain, position metamerism and functional isomerism. Ethers are functional isomers of alcohols.
- (g) In IUPAC system ethers are called as 'Alkoxy alkane'.
- (h) Ethers are compounds of the general formula  $R-O-R$ ,  $Ar-O-R$  or  $Ar-O-Ar$ , where  $Ar$  is an aromatic group.
- (i) An ether is symmetrical if the two groups attached to the oxygen atom are the same, and it is unsymmetrical if the groups are different.



### PREPARATION

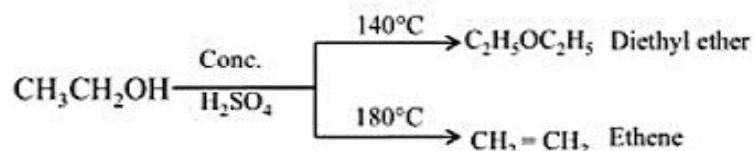
#### 1. Dehydration of alcohols



A water molecule is lost for every pair of alcohol molecules. Dehydration is limited to the preparation of symmetrical ethers, because a combination of two different alcohols yields a mixture of three ethers.

Alcohols can also dehydrate to alkenes, but dehydration to ethers is controlled by the choice of reaction conditions.

Example:

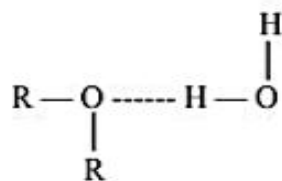


Ether formation by dehydration is an example of nucleophilic substitution: protonated alcohol is the substrate and the second molecule of alcohol is the nucleophile.

The reaction is  $S_N^1$  for  $2^\circ$  and  $3^\circ$  alcohols and  $S_N^2$  for  $1^\circ$  alcohol.



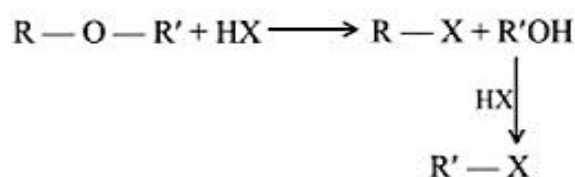




## CHEMICAL PROPERTIES

Ethers are unreactive compounds. The ether linkage is quite stable towards bases, oxidising, and reducing agents.

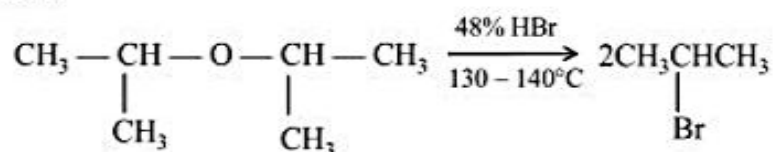
### 1. Cleavage by acids



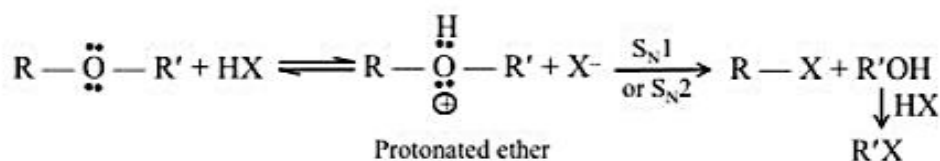
Reactivity of HX :  $\text{HI} > \text{HBr} > \text{HCl}$ .

Cleavage takes place under vigorous conditions using concentrated acids and high temperature.

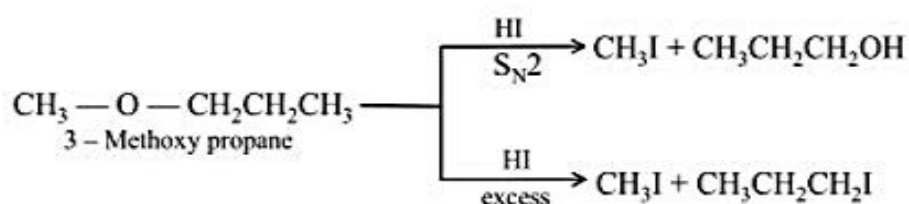
A dialkyl ether initially yields an alkyl halide and an alcohol; the alcohol may further react to form second mole of alkyl halide.

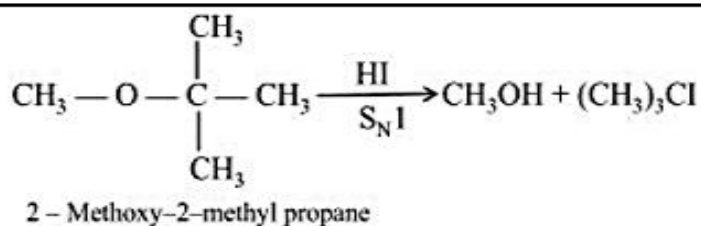


The initial reaction between an ether and an acid results in the formation of a protonated ether. The cleavage then involves a nucleophilic attack by a halide ion on this protonated ether with the displacement of the weakly basic alcohol molecule.



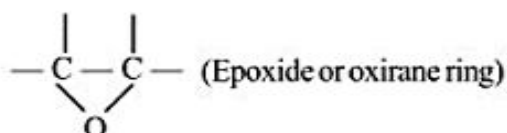
A primary alkyl group tends to undergo  $\text{S}_{\text{N}}2$  displacement and a tertiary alkyl group tends to undergo  $\text{S}_{\text{N}}1$  displacement.



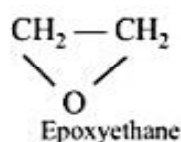
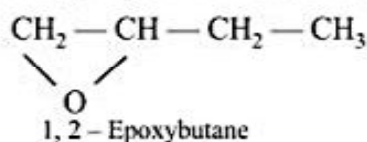


## Epoxides

Epoxides are compounds containing the three-membered ring.

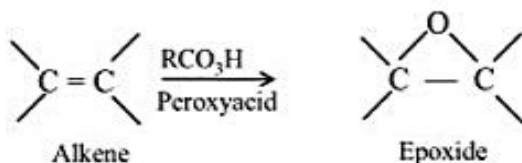


Epoxides belong to a class of compounds called cyclic ethers. The three-membered ring makes epoxides an exceedingly important class of compounds.

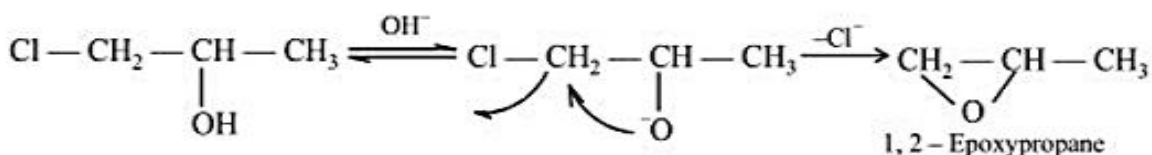


## PREPARATION

Epoxides are commonly obtained by oxidation of alkenes by peroxy acids.

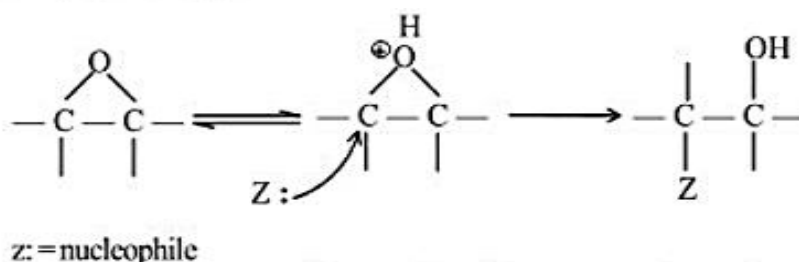


Silver oxide can also oxidise alkenes to epoxides. An internal  $\text{S}_{\text{N}}2$  reaction in a chlorohydrin can be used to prepare three membered cyclic ethers.

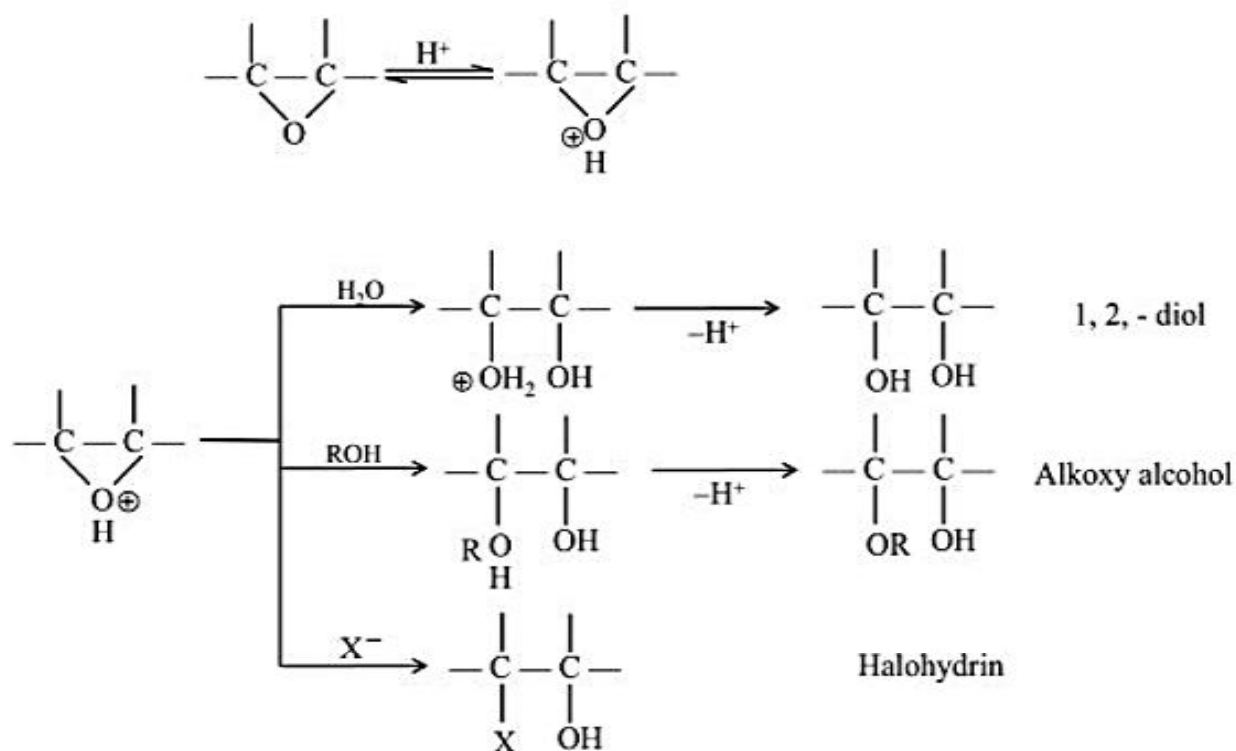


**Reactions :** Epoxides have highly strained three-membered rings that can undergo acid- or base-catalysed ring cleavage.

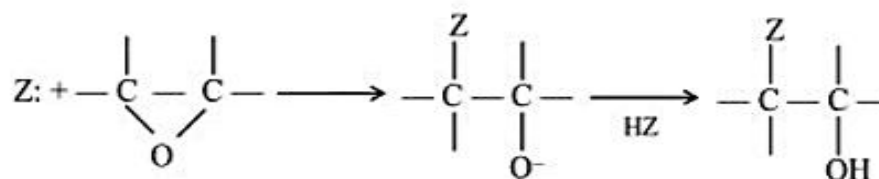
### 1. Acid-catalysed cleavage



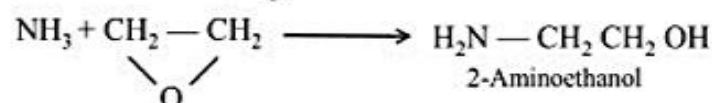
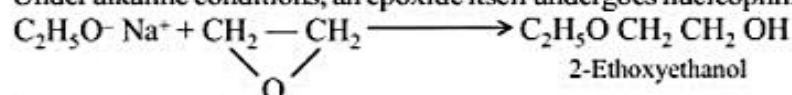
At first, the epoxide is protonated by an acid and the protonated epoxide can then undergo an attack by nucleophilic reagents.



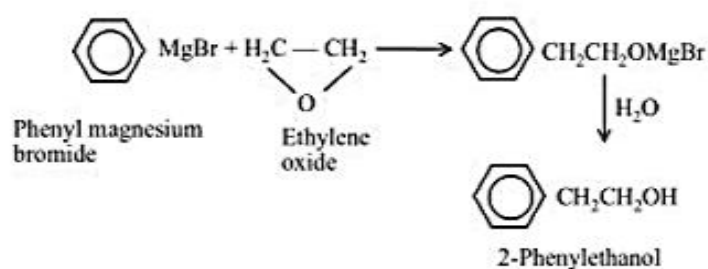
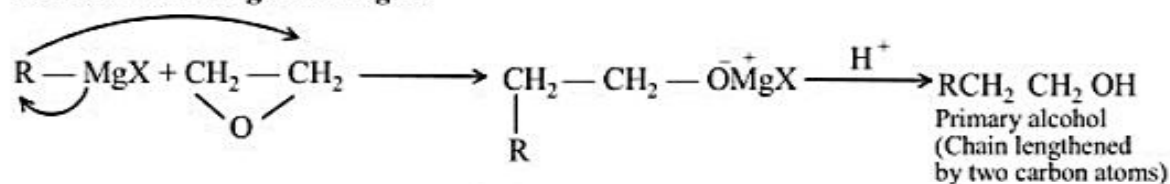
## 2. Base-catalysed cleavage



Under alkaline conditions, an epoxide itself undergoes nucleophilic attack.



## 3. Reaction with Grignard reagent



## MCQ

- Q.1 Ethyl iodide reacts with moist  $\text{Ag}_2\text{O}$  to form –  
 (A) Ether (B) Alcohol (C) Alkene (D) Alkane
- Q.2 Ethyl iodide reacts with sodium ethoxide to form –  
 (A) Ethene (B) Ethoxy ethane (C) Alcohol (D) None
- Q.3 Ether reacts with halogen in dark and in light to give –  
 (A) Same products (B) Different products  
 (C) It does not react in light (D) It does not react in dark
- Q.4 Ether reacts with  $\text{PCl}_5$  to form –  
 (A) Ethyl chloride (B) Phosphorous oxy trichloride  
 (C) Both (A) & (B) (D) None
- Q.5 An example of a compound with functional group — O — is -  
 (A) Acetic acid (B) Methyl alcohol (C) Diethyl ether (D) Acetone
- Q.6 An organic compound A reacts with sodium metal and forms B. On heating with conc.  $\text{H}_2\text{SO}_4$ , A gives diethyl ether. So A and B are -  
 (A)  $\text{C}_3\text{H}_7\text{OH}$  and  $\text{CH}_3\text{ONa}$  (B)  $\text{CH}_3\text{OH}$  and  $\text{CH}_3\text{ONa}$   
 (C)  $\text{C}_4\text{H}_9\text{OH}$  and  $\text{C}_4\text{H}_9\text{ONa}$  (D)  $\text{C}_2\text{H}_5\text{OH}$  and  $\text{C}_2\text{H}_5\text{ONa}$
- Q.7 In the presence of an acid catalyst, two alcohol molecules will undergo dehydration to give -  
 (A) Ester (B) Anhydride  
 (C) Ether (D) Unsaturated hydrocarbon
- Q.8 A carbon compound A forms B with sodium metal and again A forms C with  $\text{PCl}_5$ , but B and C form diethyl ether. Therefore A, and B and C are -  
 (A)  $\text{C}_2\text{H}_5\text{OH}$ ,  $\text{C}_2\text{H}_5\text{ONa}$ ,  $\text{C}_2\text{H}_5\text{Cl}$  (B)  $\text{C}_2\text{H}_5\text{Cl}$ ,  $\text{C}_2\text{H}_5\text{ONa}$ ,  $\text{C}_2\text{H}_5\text{OH}$   
 (C)  $\text{C}_2\text{H}_5\text{OH}$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_2\text{H}_5\text{Cl}_2$  (D)  $\text{C}_2\text{H}_5\text{OH}$ ,  $\text{C}_2\text{H}_5\text{Cl}$ ,  $\text{C}_2\text{H}_5\text{ONa}$
- Q.9 When ethyl iodide is treated with dry silver oxide, it forms -  
 (A) Ag (B)  $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$  (C)  $\text{C}_2\text{H}_5\text{OH}$  (D)  $\text{COOH} - \text{COOH}$
- Q.10 C—O—C bond angle in diethyl ether is about-  
 (A)  $180^\circ$  (B)  $110^\circ$  (C)  $150^\circ$  (D)  $90^\circ$

## ANSWER KEY

- Q.1 (B) Q.2 (B) Q.3 (B) Q.4 (C) Q.5 (C) Q.6 (D)  
 Q.7 (C) Q.8 (A) Q.9 (B) Q.10 (B)



## PHENOL ( $C_6H_5OH$ )

Phenol is also known as carbolic acid or Benzenol or hydroxy benzene.

In phenol –OH group is attached to  $sp^2$  – hybridised carbon.

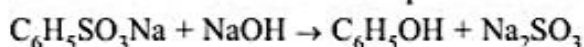
It was discovered by Runge in the middle oil fraction of coaltar distillation and named it carbolic acid (carbo = coal; oleum = oil)

It is also present in traces of human urine.

### METHODS OF PREPARATION

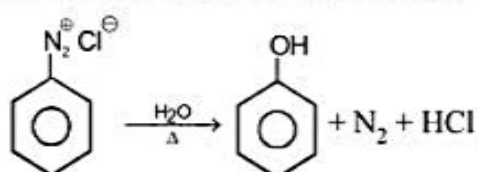
**[1] From Benzene sulphonic acid :**

When sodium salt of benzene sulphonic acid is fused with NaOH phenol is obtained.

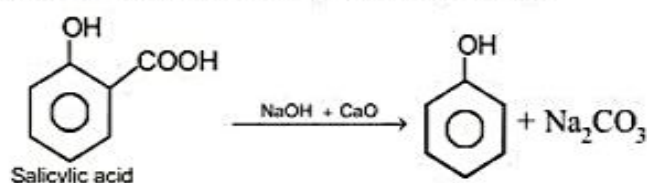


**[2] From benzene diazonium chloride :**

When benzene diazonium chloride solution is warmed phenol is obtained with evolution of nitrogen.



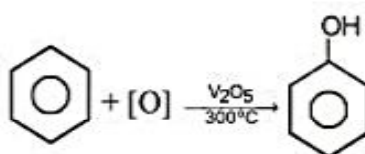
**[3] By distilling a phenolic acid : with sodalime (decarboxylation) :**



**[4] From Grignard reagent :** The grignard reagent on reaction with oxygen and subsequent hydrolysis by acid yields phenol

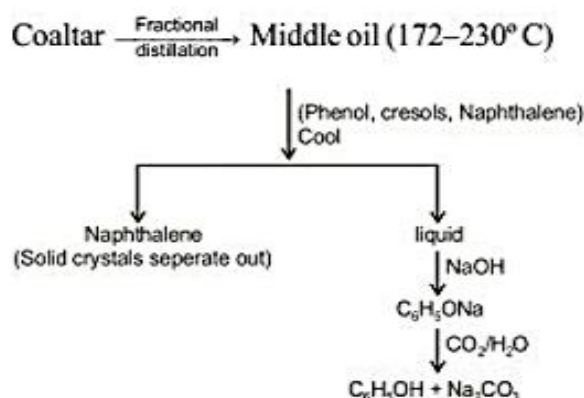
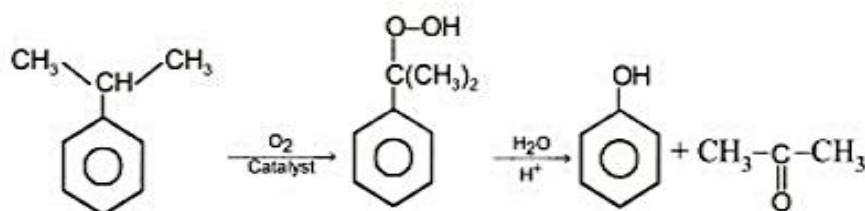
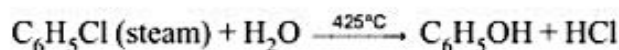
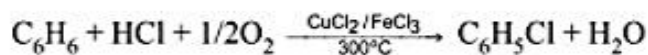
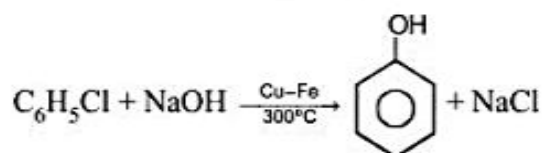


**[5] From benzene :**

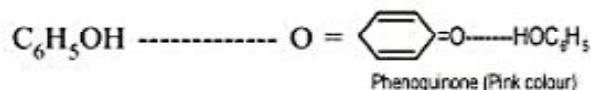


**[6] Industrial preparation of phenol :** Phenol can be prepared commercially by :

- [a] Middle oil fraction of coaltar distillation
- [b] Raschig process
- [c] Dow's process
- [d] Cumene

**[a] Middle oil fraction of coaltar :****[b] From cumene : (Isopropyl benzene) :** Cumene is oxidised with oxygen in to cumene hydro peroxide in presence of a catalyst. This is decomposed by dil.  $\text{H}_2\text{SO}_4$  in to phenol and acetone.**[c] Raschig process :** Chlorobenzene is formed by the interaction of benzene  $\text{HCl}$  and air at 300°C in presence of catalyst  $\text{CuCl}_2 + \text{FeCl}_3$ . It is hydrolysed by superheated steam at 425°C to form phenol and  $\text{HCl}$ .**[d] Dow process :** This process involves alkaline hydrolysis of chloro benzene**PHYSICAL PROPERTIES**

- Phenol is a colourless, hygroscopic crystalline solid.
- It attains pink colour on exposure to air and light.



- It is poisonous in nature but acts as antiseptic and disinfectant.
- Phenol is slightly soluble in water, readily soluble in organic solvents.
- Solubility of phenol in water is much lower than alcohols because of larger hydrocarbon part in the molecule.
- Due to intermolecular H-Bonding, phenol has relatively high B.P. than the corresponding hydrocarbons, aryl halides etc.

## CHEMICAL PROPERTIES

Chemical properties of phenol are classified in the following four categories.

Reactions of —H atom of —OH group.

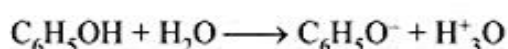
Reactions of —OH group of phenol.

Reactions of Benzene ring.

Other Reactions.

### Reactions of —H atom of —OH group

**Acidic Nature :** Phenol is a weak acid. The acidic nature of phenol due to formation of stable phenoxide ion in solution.

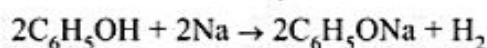


The phenoxide ion is stable due to resonance.

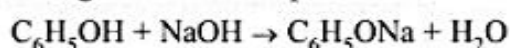
- The negative charge is spread through out the benzene ring which is stabilising factor in the phenoxide ion.
- Electron withdrawing groups ( $-\text{NO}_2$ ,  $-\text{Cl}$ ) increase the acidity of phenol while electron releasing groups ( $-\text{CH}_3$  etc.) decrease the acidity of phenol.
- Phenol is stronger acid than alcohols but weaker than the carboxylic acids and even carbonic acid.
- The acidic nature of phenol is observed in the following :

[i] Phenol changes blue litmus to red.

[ii] Highly electropositive metals react with phenol.



[iii] Phenol reacts with strong alkalis to form phenoxides

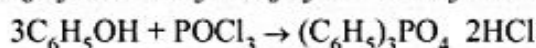
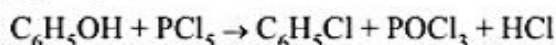


[vi] However phenol does not decompose  $\text{Na}_2\text{CO}_3$  or  $\text{NaHCO}_3$  because phenol is weaker acid than carbonic acid.

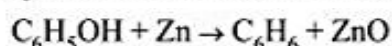


### Reaction due to —OH group :

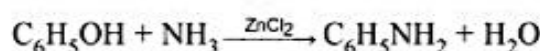
[1] **Reaction with  $\text{PCl}_5$  :** Phenol reacts with  $\text{PCl}_5$  to form chloro benzene. The yield of chlorobenzene is poor and mainly triphenyl phosphate is formed.



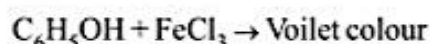
[2] **Reaction with Zn dust :** When phenol is distilled with zinc dust benzene is obtained.



[3] **Reaction with  $\text{NH}_3$  :** Phenol reacts with  $\text{NH}_3$  in presence of anhydrous  $\text{ZnCl}_2$  to form aniline.

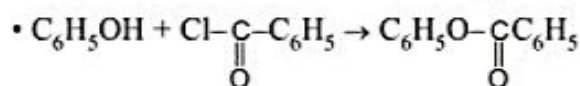
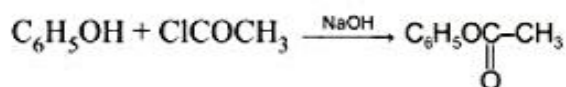


[4] **Reaction with  $\text{FeCl}_3$  :** Phenol gives violet colouration with  $\text{FeCl}_3$  solution (neutral) due to formation of a complex.



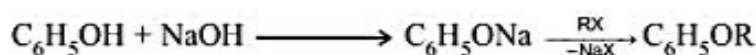
- This reaction is used to differentiate phenol from alcohols.

- [5] **Acetylation** : Phenol reacts with acid chlorides or acid anhydrides in alkali solution to form phenyl esters.



This reaction is called **Schotten-Baumann reaction**.

- [6] **Ether Formation** : Phenol reacts with alkyl halides in alkali solution to form phenyl ethers.

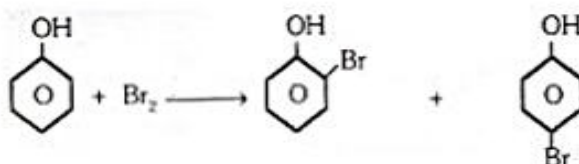


- [7] **Reaction with  $\text{P}_2\text{S}_5$**  :

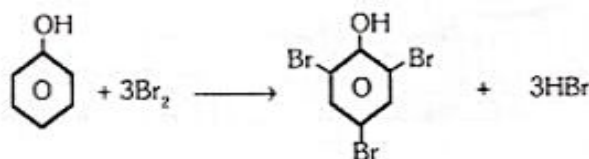


**Reaction of Benzene Ring** : The  $-\text{OH}$  group is ortho and para directing. It activates the benzene nucleus.

- [1] **Halogenation** : Phenol reacts with bromine in  $\text{CCl}_4$  to form mixture of o- and p-bromo phenol.

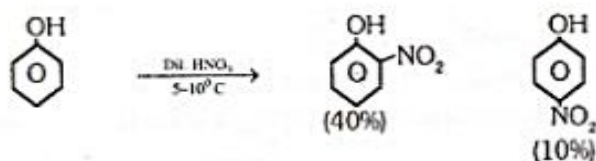


- Phenol reacts with bromine water to form a white ppt. of 2, 4, 6 tribromo phenol.



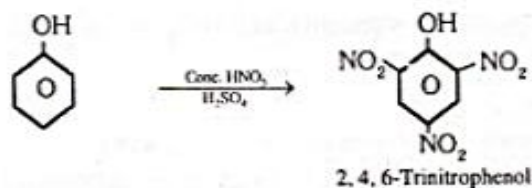
- [2] **Nitration** :

[a] Phenol reacts with dil.  $\text{HNO}_3$  at  $5-10^\circ\text{C}$  to form o- and p- nitro phenols.

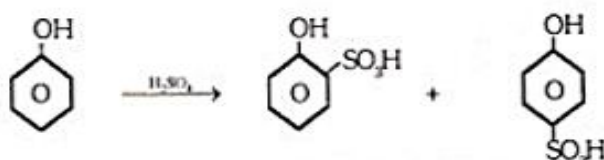


[b] When phenol is treated with conc.  $\text{HNO}_3$  in presence of conc.  $\text{H}_2\text{SO}_4$  2,4,6-trinitro phenol (picric acid) is formed.

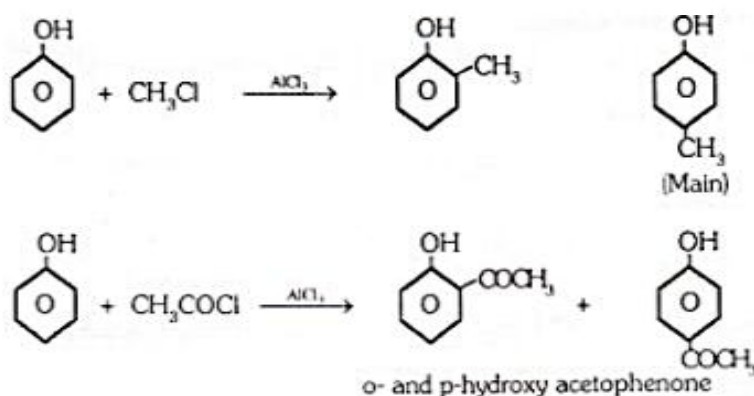




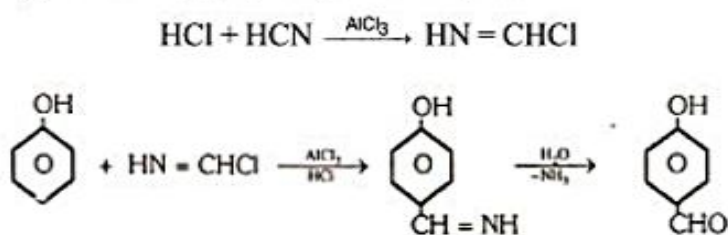
- [3] **Sulphonation** : Phenol reacts with conc.  $\text{H}_2\text{SO}_4$  to form mixture of o- and p-hydroxy benzene sulphonic acid.



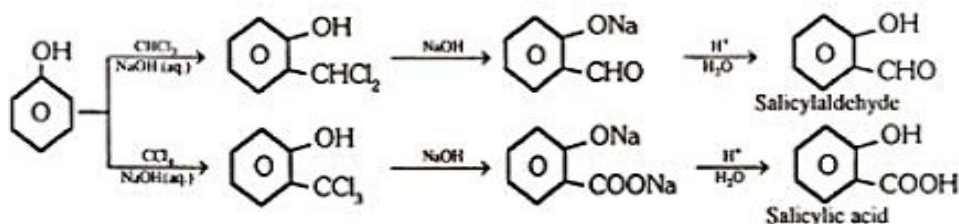
- [4] **Friedel–Craft’s reaction** : Phenol when treated with methyl chloride in presence of anhydrous  $\text{AlCl}_3$  p-cresol is main product.



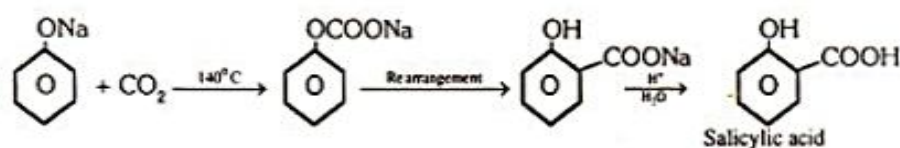
- [5] **Gattermann aldehyde synthesis** : When phenol is treated with liquid  $\text{HCN}$  and  $\text{HCl}$  gas in presence of anhydrous  $\text{AlCl}_3$  yields mainly p-hydroxy benzaldehyde.



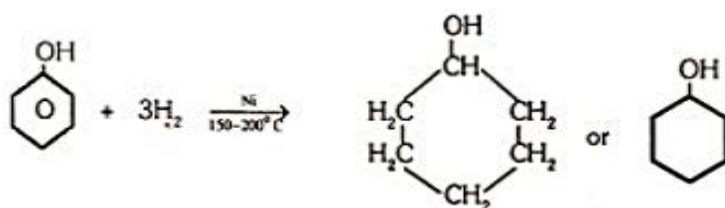
- [6] **Reimer–Tiemann reaction** : Phenol on refluxing with chloroform and  $\text{NaOH}$  (aqueous) followed by acid hydrolysis yields o-hydroxy benzaldehyde. When  $\text{CCl}_4$  is used salicylic acid is formed.



- [7] **Kolbe's Schmidt reaction :** This involves the reaction of  $\text{C}_6\text{H}_5\text{ONa}$  with  $\text{CO}_2$  at  $140^\circ\text{C}$  followed by acid hydrolysis salicylic acid is formed.

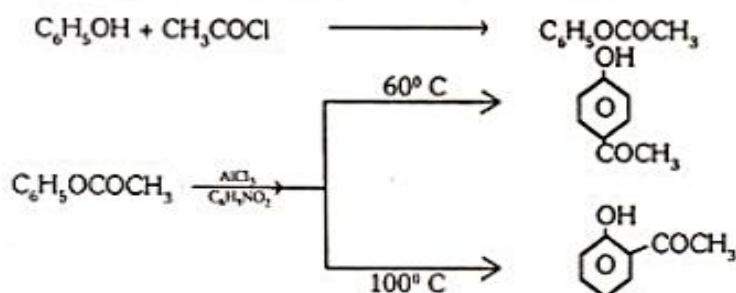


- [8] **Hydrogenation :** Phenol when hydrogenated in presence of Ni at  $150\text{--}200^\circ\text{C}$  forms cyclohexanol.

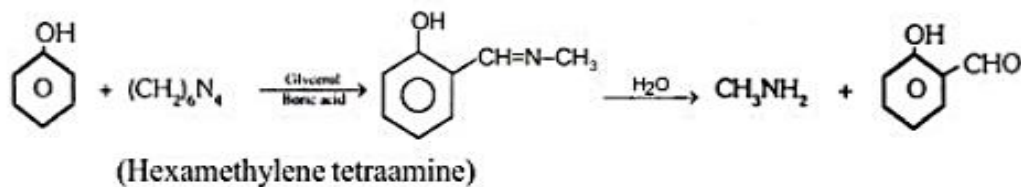


- [9] **Fries rearrangement reaction :**

When phenyl ester is heated in nitrobenzene solution, in the presence of anhyd.  $\text{AlCl}_3$  then rearrangement takes place in which acyl group is transferred at o - & p-positions of phenolic group. Up to  $60^\circ\text{C}$ , para product is obtained mainly and above  $160^\circ\text{C}$  ortho products are obtained as major product.

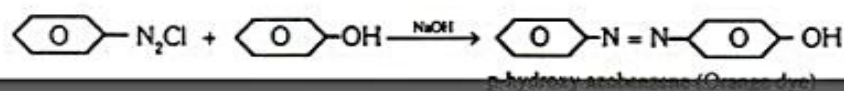


- [10] **Duff's reaction :**

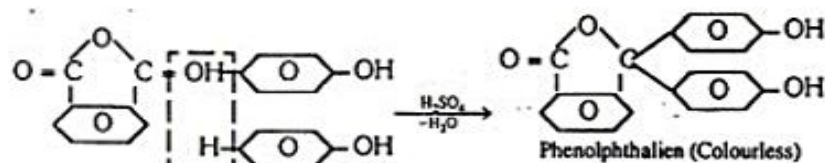


- [11] **Coupling reactions :**

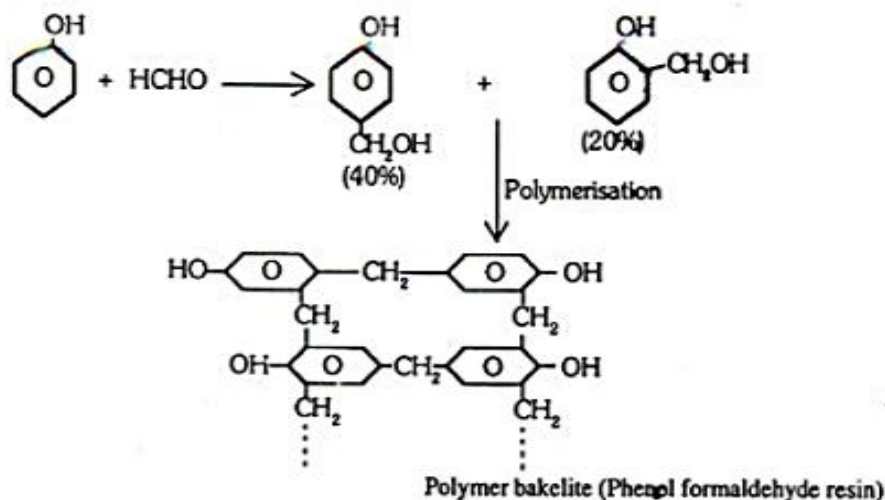
- [a] Phenol couples with benzene diazonium chloride in presence of an alkaline solution to form a dye (p-hydroxy azobenzene)



- [b] Phenol couples with phthalic anhydride in presence of conc.  $\text{H}_2\text{SO}_4$  to form a dye (phenolphthalein)

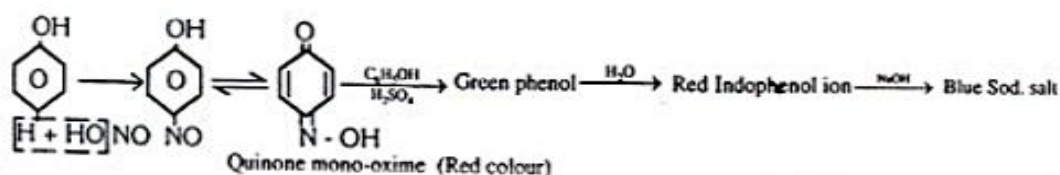


- [12] **Condensation with formaldehyde :** Phenol condenses with  $\text{HCHO}$  (excess) in presence of  $\text{NaOH}$  to form a polymer known as bakelite.

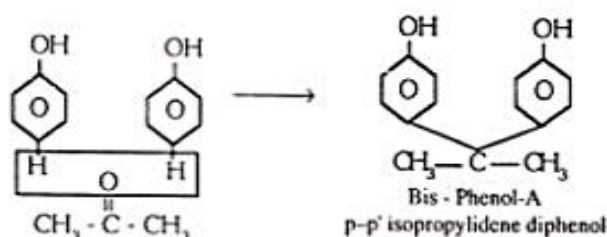


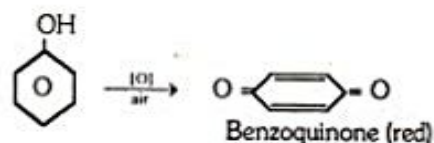
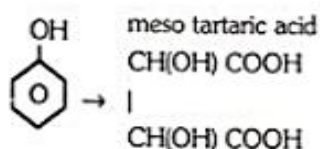
- [13] **Liberman's nitroso reaction :** When phenol is reacted with  $\text{NaNO}_2$  and conc.  $\text{H}_2\text{SO}_4$  it gives a deep green or blue colour which changes to red on dilution with water. When made alkaline with  $\text{NaOH}$  original green or blue colour is restored.

The reaction is used as a test of phenol.

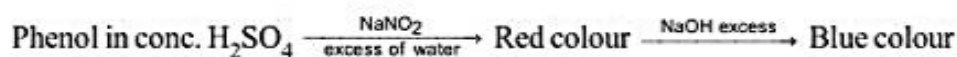


- [14] **Reaction with acetone :**



**[15] Oxidation :****[1] In presence of air :****[2]  $\text{KMnO}_4$  :****Test of Phenol :**

- [1] Phenol turns blue litmus to red.
- [2] Aqueous solution of phenol gives a violet colour with a drop of ferric chloride.
- [3] Phenol gives Lieber mann's nitroso test.



- [4] Aqueous solution of phenol gives a white ppt. of 2,4,6 tribromophenol with bromine water.
- [5] Phenol combines with phthalic anhydride in presence of conc.  $\text{H}_2\text{SO}_4$  to form phenolphthalein which gives pink colour with alkali.
- [6] With ammonia and sodium hypochlorite, phenol gives blue colour.

**Differences between phenol and alcohol ( $\text{C}_2\text{H}_5\text{OH}$ ) :**

- [1] Phenol is more acidic than aliphatic alcohol due to resonance in phenoxide ion.
- [2] Phenol gives violet colour with  $\text{FeCl}_3$  while aliphatic alcohol does not give.
- [3] Phenol gives triphenyl phosphate with  $\text{PCl}_5$  while aliphatic alcohol gives alkyl chloride.
- [4] Phenol has phenolic odour whereas alcohol has pleasant odour.
- [5] Phenol on oxidation gives quinone while alcohol gives aldehyde or ketone and acids.

**Uses of Phenol :**

Phenol is used :

- [1] As an antiseptic in soaps and lotions.
- [2] In manufacture of azodyes, phenolphthalein, picric acid (explosive), cyclohexanol (Solvent for rubber), plastic (bakelite) etc.
- [3] In manufacture of drugs like aspirin salol, phenacetin etc.
- [4] As preservation for ink.



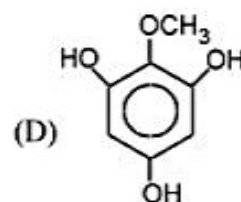
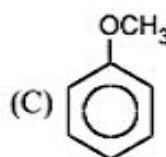
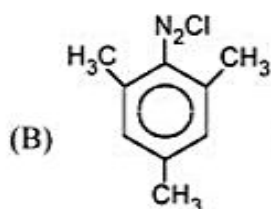
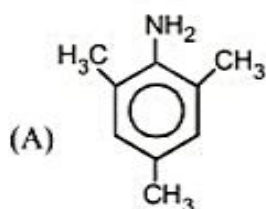
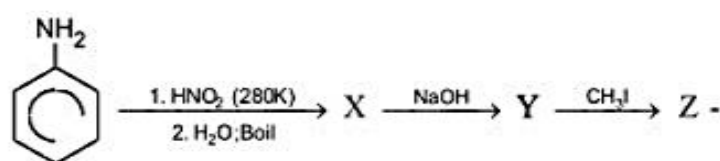
S.No.	Test/Reaction	Alcohol	Phenol
1.	Litmus test	No Reaction	Blue litmus red
2.	$\text{FeCl}_3$ Solution	No Reaction	Violet colour
3.	Benzene diazonium salt	No Reaction	Yellow or orange azo dye
4.	$\text{Br}_2$ water	No Reaction	2, 4, 6-tribromophenol

### MCQ

**Q.1** In chlorobenzene, the — Cl group -

- (A) Activates the benzene ring more, via resonance effect than deactivating it via inductive effect.  
 (B) Deactivates the benzene ring more, via inductive effect than activating it via resonance effect.  
 (C) Activates the benzene ring via resonance effect and deactivates it via inductive effect. Both these effect are evenly matched.  
 (D) It is a net deactivating group with director characteristics.

**Q.2** Identify 'Z' in the reaction given below -



**Q.3** The correct order of reactivity towards electrophilic substitution is -

- (A) Phenol > Benzene > Chlorobenzene > Benzoic acid  
 (B) Benzoic acid > Chlorobenzene > Benzene > Phenol  
 (C) Phenol > Chlorobenzene > Benzene > Benzoic acid  
 (D) Benzoic acid > Phenol > Benzene > Chlorobenzene

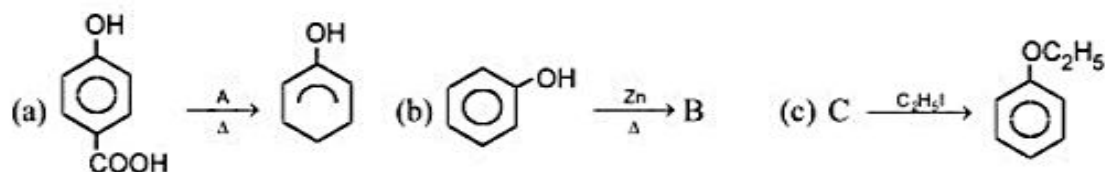
**Q.4** Which among the following is the strongest o-, p-directing group in benzene is -

- (A) —OH (B) —Cl (C) —OCH<sub>3</sub> (D) —CH<sub>3</sub>

**Q.5** The compound represented by the molecular formula  $\text{C}_7\text{H}_8\text{O}$  are -

- (A) Only alcohol (B) Only ether  
 (C) Only phenolic compound (D) All the three types of compounds

Q.6 Identify A, B, and C in the following reactions—



- (A) Sodalime, benzene, potassium phenoxide  
 (B) Zn, benzene, sodium ethoxide  
 (C) Zn, cyclohexanone, sodium ethoxide  
 (D) None of the above

Q.7 Water insoluble aromatic compound dissolves in sodium hydroxide but remain insoluble in sodium bicarbonate. Hence the expected compound should be - [where  $\phi = C_6H_5$ ]

- (A)  $\phi-COOH$  (B)  $\phi-OH$  (C)  $\phi-CO-CH_3$  (D)  $\phi-NH_2$

Q.8 Salicylaldehyde and o-nitrophenol are less soluble in water because -

- (A) Their molecular weights are high (B) They exhibit intra molecular H-bonding  
 (C) They are aromatic compounds (D)  $-CHO$  and  $-NO_2$  groups are not polar

Q.9 Rate of substitution reaction in phenol is -

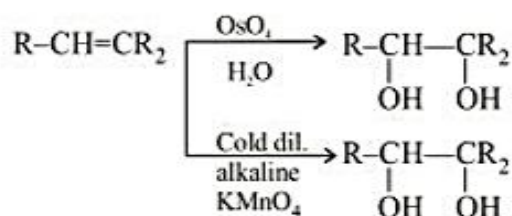
- (A) Slower than the rate of benzene (B) Faster than the rate of benzene  
 (C) Equal to the rate of benzene (D) None

#### ANSWER KEY

- |     |     |     |     |     |     |     |     |     |     |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Q.1 | (B) | Q.2 | (C) | Q.3 | (A) | Q.4 | (A) | Q.5 | (D) |
| Q.6 | (A) | Q.7 | (B) | Q.8 | (B) | Q.9 | (B) |     |     |

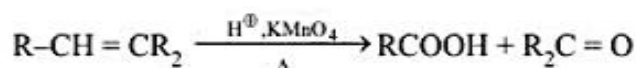
## OXIDATION OF ALKENES, ALCOHOLS & CARBONYL COMPOUNDS

### (I) OXIDATION OF ALKENES



- Cold dil. alkaline  $\text{KMnO}_4$  is called as Bayer's reagent.
- Overall syn addition
- Given by alkenes & alkynes
- Benzene & Cyclopropane can not give this reaction.

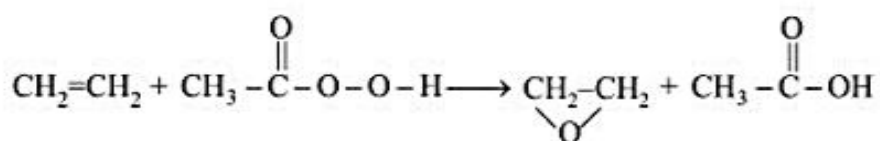
If we use acidic  $\text{KMnO}_4$  or warm  $\text{KMnO}_4$  or too concentrated  $\text{KMnO}_4$  the oxidative cleavage of Glycol occurs resulting in mixture of Carboxylic acids & Ketones.



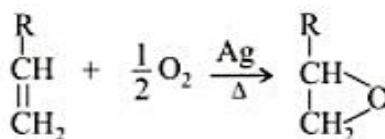
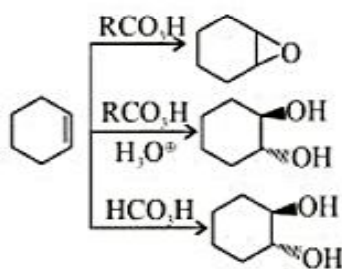
Hot acidic  $\text{KMnO}_4$ , Hot acidic  $\text{K}_2\text{Cr}_2\text{O}_7$  & hot acidic  $\text{NaIO}_4$  gives same result with alkene. The effect is similar to that of oxidative ozonolysis on alkenes.

#### Preilschaive reaction :

Epoxidation of alkenes is reaction of alkenes with peroxyacids.



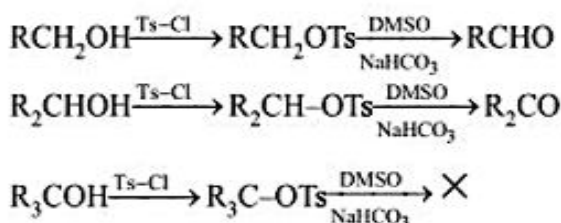
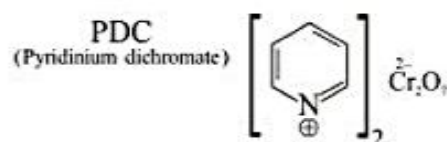
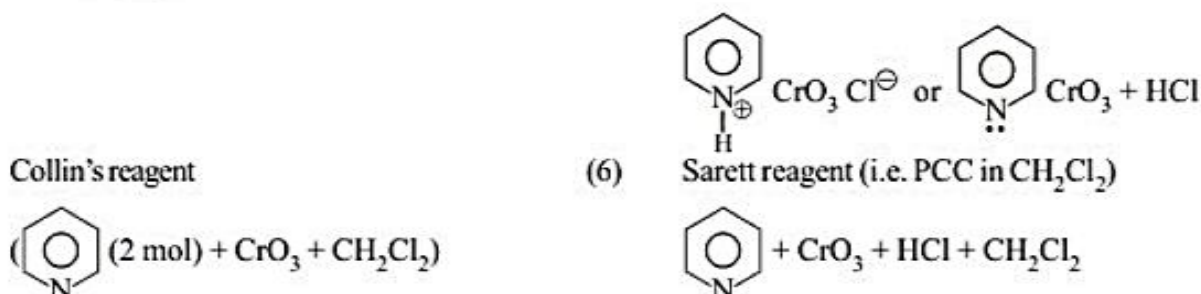
- With the decrease in nucleophilicity of double bond, rate of reaction decreases.
- With the decrease in  $e^-$  withdrawing substituents in leaving group, rate decreases.



## (II) OXIDATION OF ALCOHOLS

### Oxidising agents

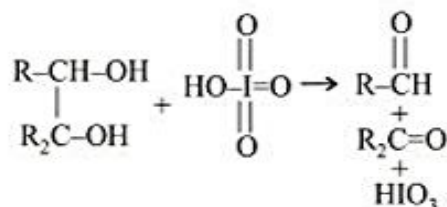
- (1)  $\text{Cu} / 300^\circ\text{C}$  (or Red hot Cu tube)
- (2)  $\text{H}^+/\text{KMnO}_4, \Delta$  (Strong oxidising agent)
- (3)  $\text{H}^+/\text{K}_2\text{Cr}_2\text{O}_7, \Delta$  (Strong oxidising agent)
- (4) PCC (Pyridinium chloro chromate)
- (5) Collin's reagent
- (6) Sarett reagent (i.e. PCC in  $\text{CH}_2\text{Cl}_2$ )
- (7) PDC (Pyridinium dichromate)
- (8) Jones reagent ( $\text{H}_2\text{CrO}_4$  in Anhydrous acetone)
- (9)  $\text{TsCl} + \text{DMSO} + \text{NaHCO}_3$
- (10)  $\text{MnO}_2$ -Oxidises only allylic or benzylic-OH i.e.
- (11) **Periodic cleavage**  
A similar oxidation is obtained in case of  $\text{HIO}_4$  known as periodic cleavage.
- (12) NBS
- (13) **Openaur oxidation**



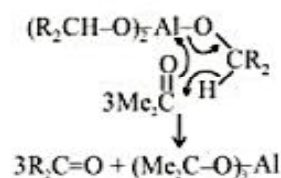
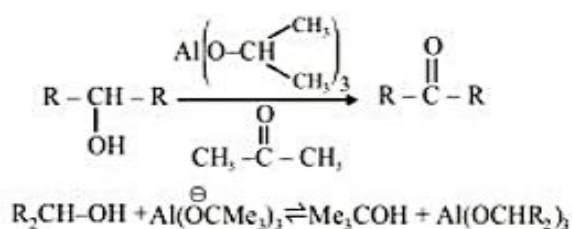
or  $\text{CrO}_3 + \text{H}_2\text{SO}_4$  in acetone.  
Sufficiently mild so that it oxidises alcohols without oxidising or rearranging double bonds (8 or 9)

$1^\circ$  Allylic or benzylic OH  $\xrightarrow{\text{MnO}_2}$  Aldehyde  
 $2^\circ$  Allylic or benzylic OH  $\xrightarrow{\text{MnO}_2}$  Ketone

No effect on  $3^\circ$  ROH and on Carbon-carbon multiple bond.



But reaction is only observed for cis Vic-diols.

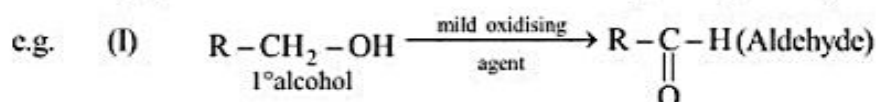


Oxidation of alcohol with aluminium tertiary butoxide is Openaur oxidation.

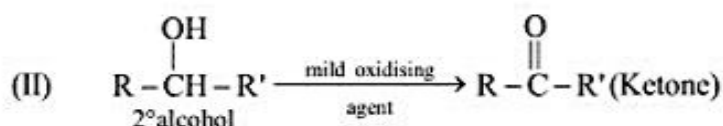




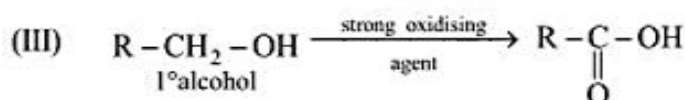
Different oxidising agents are used to oxidise alcohols in corresponding carbonyl compounds and carboxylic acids.



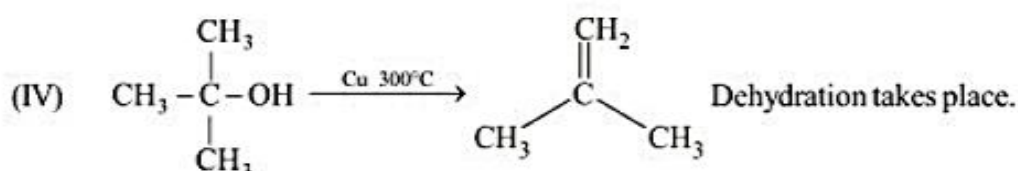
Oxidation agent : 1,4,5,6,7,8,9,12



Oxidation agent : 1,2,3,4,5,6,7,8,9,12,13



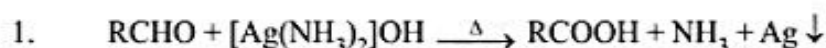
Oxidation agent : 2,3



(V) Double bond or Triple bond is not affected by 1,4,5,6,7,8,9,10

(VI) No effect on 3° alcohol by 2,3,4,5,6,7,8,9,10,12,13

### (III) OXIDATION OF CARBONYL COMPOUNDS

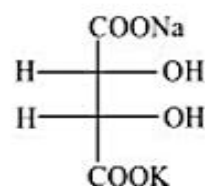


Aldehyde acts as reducing agent, they can reduce mild oxidizing agents like Tollen's Reagent. Tollen's test Gentle Heating for 20 to 25 mins.

2. **Fehling's Solutions**

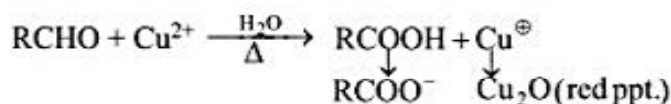
Fehling's A  
aq.  $\text{CuSO}_4$

Fehling's B  
Alk. solution of Roschelye  
salt (sodium potassium tartrate)



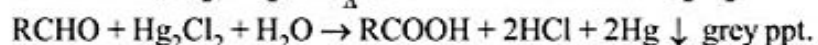
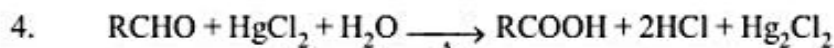
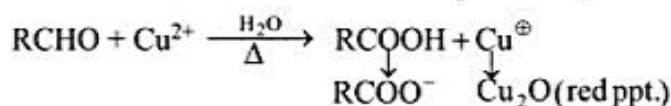
It acts a carrier for  $\text{Cu}^{2+}$  as it make reversible complex with  $\text{Cu}^{2+}$

This test is also used is Blood and Urine test.



3. **Benedict's solution**

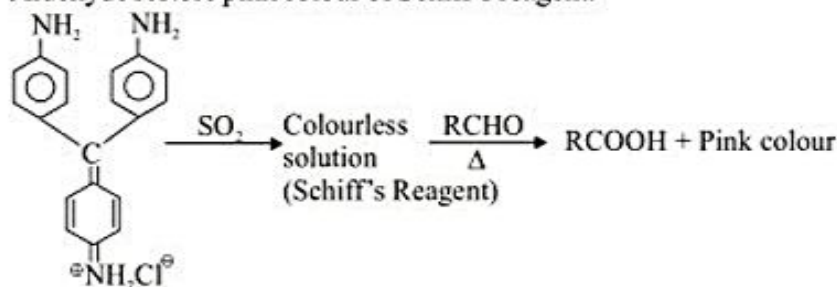
Sodium Citrate + NaOH +  $\text{NaHCO}_3$  +  $\text{CuSO}_4$



### 5. Schiff's Reagent

Schiff's Reagent is aq. solution of following base decolourised by passing  $\text{SO}_2$ .

Aldehyde restore pink colour of Schiff's reagent.



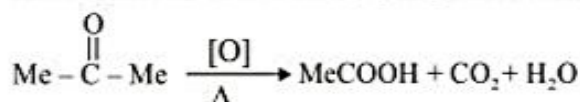
p-Rosaniline Hydrochloride

Magenta colour (Fuschin)

Ketones are not easy to oxidize so they do not give these 5 tests. These five tests can be used to distinguish aldehyde and ketones. Both gives 2,4 DNP test

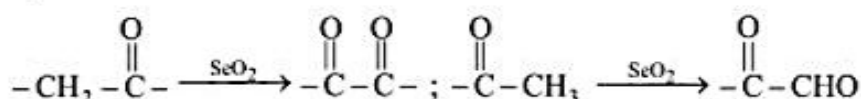
## KETONES ARE DIFFICULT TO OXIDIZE

Ketones can be oxidized from their enolic form at high temperature with very strong oxidizing agent. Oxidation of ketones is sometimes governed by **Popoff's rule**. According to this rule carbonyl group remains with the smaller alkyl group. More electron rich alkene will be easy to oxidized.

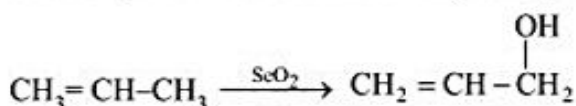


### Allylic oxidation

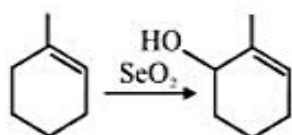
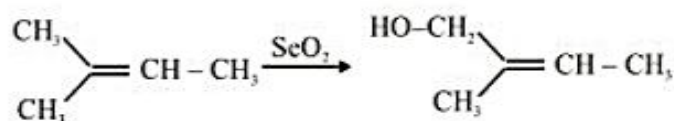
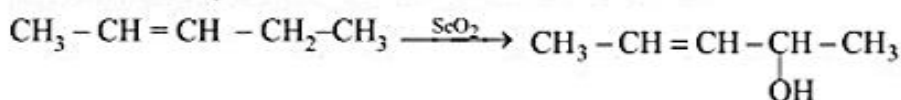
$\text{SeO}_2$  is a selective oxidizing agent with converts  $-\text{CH}_2-$  group adjacent to carbonyl group into carbonyl group. The reagent, in general, oxidises active methylene and methyl groups to ketonic and aldehydic groups respectively.



Double bonds, triple bonds and aromatic rings may also activate the methylene group. The methylene or methyl group  $\alpha$  to the most highly substituted end of the double bond is hydroxylated according to the order of preference of oxidation  $\text{CH}_2 > \text{CH}_3 > \text{CH}$  groups.



Rate of reactivity order  $2^\circ \text{C} - \text{H} > 1^\circ \text{C} - \text{H} > 3^\circ \text{C} - \text{H}$



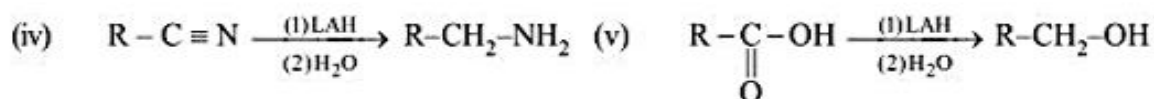
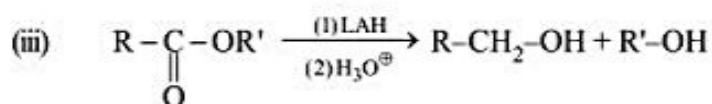
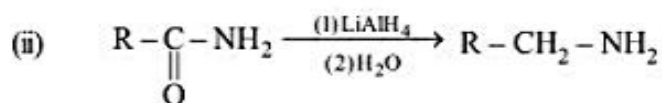
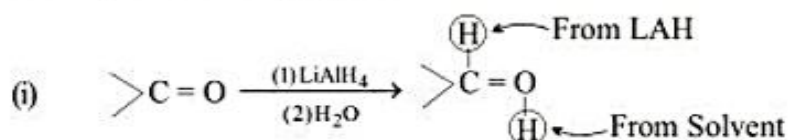
### Reducing agents and their role

Group	Product	LAH in ether	LiAlH(OCMe <sub>3</sub> ) <sub>3</sub> in THF	NaBH <sub>4</sub> in EtOH	H <sub>2</sub> <sup>+</sup> ** catalyst
-CHO	-CH <sub>2</sub> OH	+	-	+	+
>C=O	>CH-OH	+	-	+	+
-CO <sub>2</sub> H	-CH <sub>2</sub> OH	+	-	-	+
-CO <sub>2</sub> R	-CH <sub>2</sub> OH	+	-	-	+
-COCl	-CH <sub>2</sub> OH	+	+	+	+
-CONH <sub>2</sub>	-CH <sub>2</sub> NH <sub>2</sub>	+	-	-	+
(RCO) <sub>2</sub> O	RCH <sub>2</sub> OH	+	-	-	+
-CN	-CH <sub>2</sub> NH <sub>2</sub>	+	-	-	+
>C=NOH	-CH <sub>2</sub> NH <sub>2</sub>	+	-	-	+
>C=C<	>CH-CH<	-	-	-	+
-C≡C-	-CH=CH-	-	-	-	+
1° RX	RH	+	-	-	+

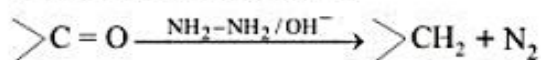
\* Product is RCHO

\*\* Catalyst : Ni / Pd / Pt / Ru

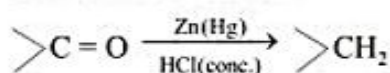
**LiAlH<sub>4</sub> as a reducing agent :**



**Wolf Kischner reduction :**



**Clemenson reduction**



## ALKYL HALIDE

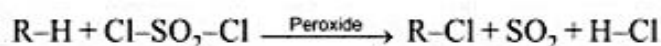
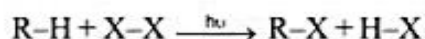
### CHARACTERISTICS

- (a) These are the organic compound in which halogen is directly linked with carbon atom.
- (b) These are also called as Haloalkane.
- (c) Their general formula is  $C_nH_{2n+1}X$ , ( $X = F, Br, Cl, I$ ).
- (d) In these compounds, hybridisation state of carbon is  $sp^3$ .
- (e) In these compounds, geometry of carbon is tetrahedral.
- (f) Central carbon atom has a bond angle of  $109^\circ 28'$ .
- (g) On the basis of no. of halogen atom, these are of following types –
  - (i) Monohalide – They possess single halogen atom.  
eg.  $CH_3 - Cl$ ,  $CH_3 - CH_2Br$
  - (ii) Dihalide – These are of three types  
eg. gem dihalide, vicinal dihalide and  $\alpha, \omega$  halide
  - (iii) Trihalide – They possess three halogen atoms.  
eg.  $CHCl_3$ ,  $CHI_3$
  - (iv) Tetrahalide – They possess four halogen atoms.  
eg.  $CCl_4$
  - (vi) Polyhalide – They possess more than four halogen atoms.
- (h) Alkyl halide shows chain and position isomerism. If unsymmetrical or chiral carbon is present then it shows optical isomerism also.

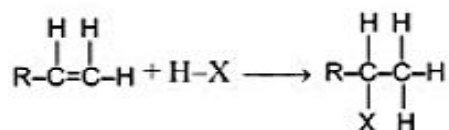
### METHODS OF PREPARATION OF ALKYL HALIDES

#### (a) By Halogenation of Alkanes

Halogenation of alkanes takes place by free radical mechanism.



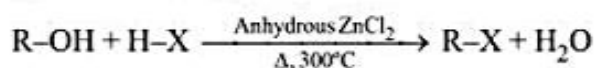
#### From Alkene (Hydrohalogenation) :-



**Note :** From alkyne we cannot obtain monoalkylhalide.

#### From Alcohol :-

##### (a) Using dry $H-X$ :-



(dry)



**Note :**

- (i) The reactivity order of HX in the above reaction is –  $\text{HI} > \text{HBr} > \text{HCl}$
- (ii) The reactivity order of alcohols in the above reaction is –  $3^\circ > 2^\circ > 1^\circ > \text{MeOH}$

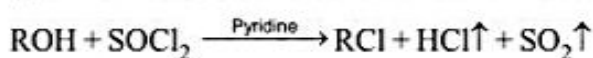
The above reaction is called as '**Grove's Process**'.

- (b) Using  $\text{PCl}_3$  :  $-3\text{ROH} + \text{PCl}_3 \longrightarrow 3\text{R}-\text{Cl} + \text{H}_3\text{PO}_3$
- (c) Using  $\text{PCl}_5$  :  $-\text{ROH} + \text{PCl}_5 \longrightarrow \text{R}-\text{Cl} + \text{HCl} + \text{POCl}_3$

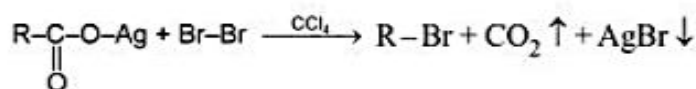
**Important Note : –**

Bromine or Iodine derivatives can not be obtained from the above reaction because due to larger size of Bromine or Iodine,  $\text{PBr}_5$  or  $\text{PI}_5$  are unstable.

- (d) Darzen's Process : – It is the best method for preparation of alkyl halide.

**From Silver Salt of Carboxylic Acid :**

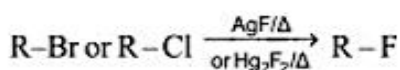
The reaction is called as '**Borodiene - Hunsdiecker**' reaction. It is also a good method for obtaining alkyl halide, but from this reaction we obtain only bromo derivatives because reaction is based upon free radical mechanism.

**Note : –**

- (i) In the above reaction the reactivity of alkyl group is :  $1^\circ > 2^\circ > 3^\circ$
- (ii) It is also an example of decarboxylation.

**From Alkyl Halide :****Finkelstein Reaction :**

In this reaction only exchange takes place and the reaction is called as Halogen exchange reaction or '**Finkelstein Reaction**'.

**Swarts reaction**

This reaction is called as '**Swarts reaction**'

**PHYSICAL PROPERTIES**

- (a) Alkyl halides are colourless with sweet smell or pleasant smell oily liquid, whereas  $\text{CH}_3\text{F}$ ,  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_3-\text{CH}_2-\text{F}$ ,  $\text{CH}_3-\text{CH}_2-\text{Cl}$  are gaseous in nature.
- (b) Alkyl halides having 18-carbon or more than it are solid in nature.

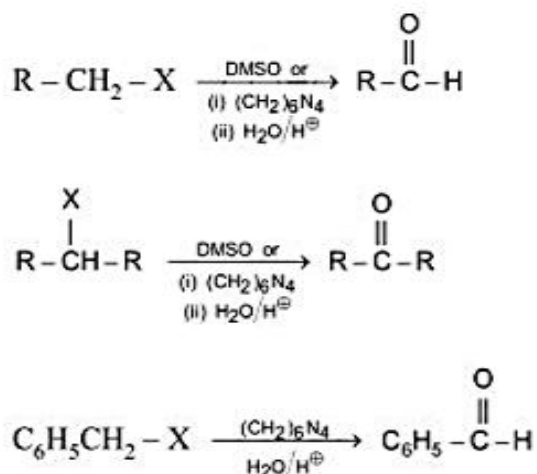
- (c) Although carbon - halogen bond is polar in nature but alkyl halides are insoluble in  $H_2O$  because they cannot form bond with  $H_2O$ .
- (d) These are completely soluble in organic solvents.
- (e) M.P & B.P.  $\propto$  molecular weight. For same alkyl group the order of B.P. is  $RI > RBr > RCl > RF$
- (f) Polarity order is  $RF > RCl > RBr > RI$
- (g) Reactivity order is  $RI > RBr > RCl > RF$
- (h) For same halide group reactivity order is  $3^\circ \text{ halide} > 2^\circ \text{ halide} > 1^\circ \text{ halide}$

Fluorides and Chlorides are lighter than water where as bromides and iodides are heavier than  $H_2O$  due to more density of bromine than oxygen.  $CH_2I_2$  is heavier liquid after Hg.

## CHEMICAL PROPERTIES

### Oxidation reaction

- (i) Only primary and secondary alkyl halides undergo oxidation. Tertiary alkyl halide does not undergo oxidation.
- (ii) Primary alkyl halides give aldehyde where as secondary alkyl halides give ketone in this reaction.
- (iii) Oxidising agent is either :
- Dimethyl sulphoxide or
  - Reaction with  $(CH_2)_6N_4$  followed by hydrolysis.
- (iv) Reactivity  $\propto$  number of  $\alpha$ -hydrogens.



- Note :** (1) Oxidation of Benzyl halides by  $(CH_2)_6N_4$  is known as **sommelet aldehyde synthesis**.
- (2) Oxidation of alkyl halide with DMSO is known as **swern oxidation**.

### Reduction :

Haloalkanes on reduction produces alkanes frequently, reduction is done as follows.



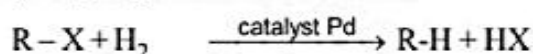
- (i) By Nascent hydrogen liberated from  $\text{Na/C}_2\text{H}_5\text{OH}$  or  $\text{Sn/HCl}$  or  $\text{Zn/HCl}$  or  $\text{Zn-Cu couple/C}_2\text{H}_5\text{OH}$  etc.



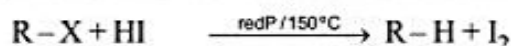
- (ii) By hydride ion  $[\text{H}^\ominus]$  liberated from  $\text{LiAlH}_4$  or  $\text{NaBH}_4$ . It is completed by nucleophilic substitution reaction.



- (iii) By catalytic hydrogenation of haloalkane -



- (iv) By reduction of  $\text{RI}$  with  $\text{HI}$  in presence of red P.

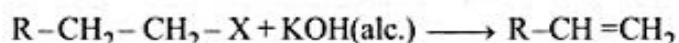


#### Reaction with $\text{KOH}$ :

- (a) With aqueous  $\text{KOH}$  : -



- (b) With alcoholic  $\text{KOH}$  : - Dehydrohalogenation takes place and alkenes are formed.

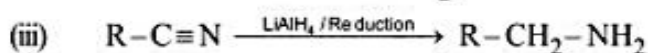
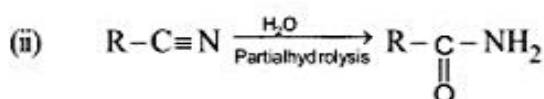
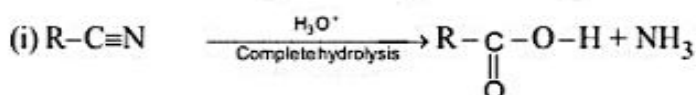


#### Reaction with $\text{KCN}$ :

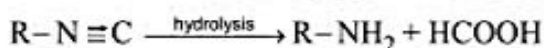


Alkane nitrile

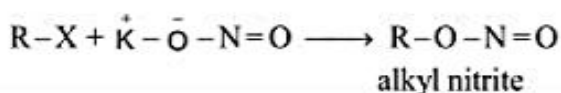
Alkane nitrile is an important compound which gives following products.

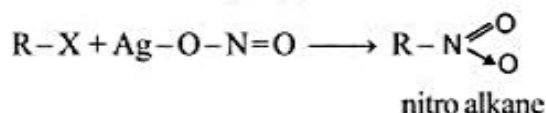
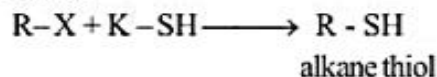
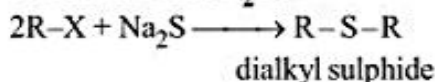
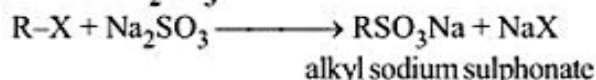


#### Reaction with $\text{AgCN}$ :



#### Reaction with $\text{KNO}_2$ :



**Reaction with  $\text{AgNO}_2$  :****Reaction with KSH :****Reaction with  $\text{Na}_2\text{S}$  :-****Reaction with  $\text{Na}_2\text{SO}_3$  :**

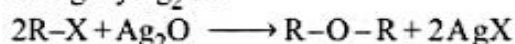
Reaction is known as "**Strecker reaction**".

**Reaction with NaOR :**

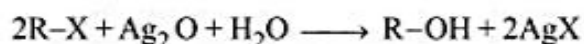
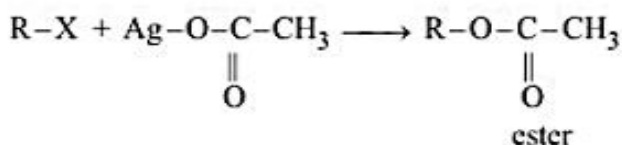
The above reaction is called as "**Williamson ether synthesis**".

**Reaction with  $\text{Ag}_2\text{O}$  :**

(a) Using dry  $\text{Ag}_2\text{O}$  :



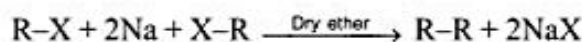
(b) Using moist  $\text{Ag}_2\text{O}$  :

**Reaction with Silver Acetate :**

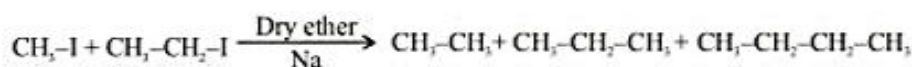
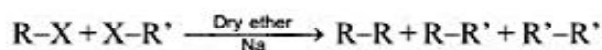
The reaction is called as '**Esterification**'.

**Coupling Reactions**

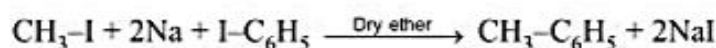
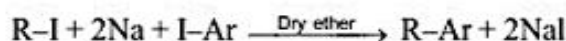
(A) **By Wurtz Reaction** : An alkane having even number of carbon atoms can be obtained by **Wurtz Reaction**.



Alkane having odd number of carbon atoms can be obtained by mixed **Wurtz Reaction**.



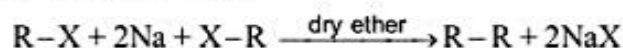
(B) **By Wurtz-Fitting Reaction**



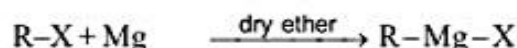


**Reaction with metals :**

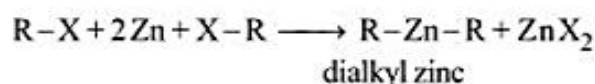
(a) With Na : – (Wurtz reaction)



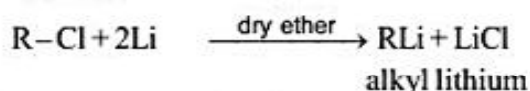
(b) With Mg : – (Grignard reaction)



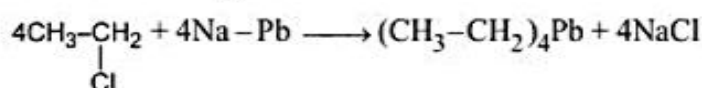
(c) With Zn dust : – (Frankland reaction)

Dialkyl zinc is known as '**Frankland - Reagent**'.

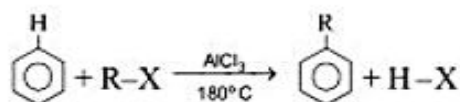
(d) With Li : –

**Note :** Alkyl lithium is more reactive than Grignard reagent.

(e) With Na-lead alloy : –



TEL (tetra ethyl lead)

**Note :** Tetra ethyl lead is used as antiknocking agent.**Reaction with Benzene :**The reaction is called as '**Friedel-craft Reaction**'.**Important Note :-** Alkyl halide shows electrophilic substitution reaction in the above reaction, which is exception in alkyl halide**Uses of Alkyl Halides**

- (i) Alkyl halides are used as **weak refrigerants**, but more suitable **freons** are now being used in place of alkyl halides.
- (ii) Synthesis of **detergents** is carried out from alkyl halides by Strecker's reaction.
- (iii) Synthesis of **antiknock compounds**.
- (iv) Alkyl halides, especially alkyl bromides and alkyl iodides are used for the synthesis of other organic compounds of almost all classes, in laboratory and in industry.
- (v) Alkyl halides are generally used as starting substances for the manufacture of **alcohols, ethers and esters**.
- (vii) Synthesis of important organometallic compounds, like Grignard's reagents. Frankland's reagents, etc., is carried out from alkyl halides.

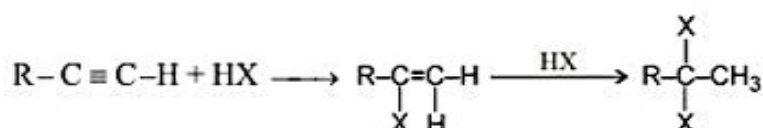
## TYPES OF DIHALIDES

Dihalides are of two types : –

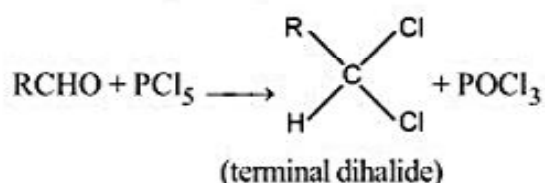
- (a) **Gem dihalide** : These are the halides in which two identical halogen atoms are attached on same carbon.
- (b) **Vicinal dihalide** : In these halides two identical halogen atoms are attached on adjacent carbon atoms.

## METHODS OF PREPARATION OF GEM DIHALIDES

- (a) From Alkyne (By hydrohalogenation) : –



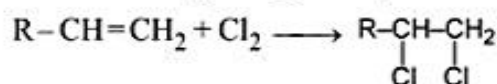
- (b) From carbonyl compounds : –



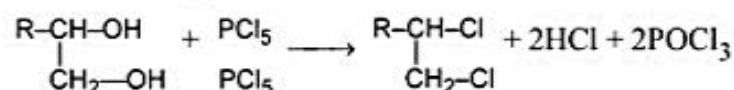
**Note** : If ketone is taken internal dihalide is formed.

## METHODS OF PREPARATION OF VICINAL DIHALIDES

- (a) From Alkene (By halogenation) : –



- (b) From Vicinal glycol : –

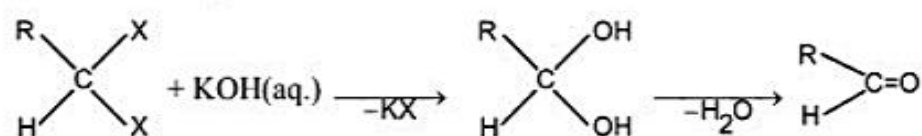


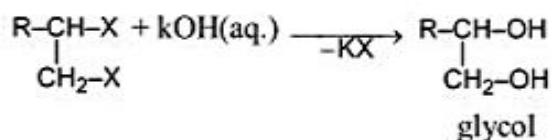
## PHYSICAL PROPERTIES OF DIHALIDES

- (a) Dihalides are colourless with pleasant smell liquid, Insoluble in water, soluble in organic solvent.
- (b) Melting point and boiling points are directly proportional to molecular mass but boiling point of vicinal dihalides are more than gem dihalides. Also, reactivity of vicinal dihalide is more than gemdihalide, but these are less reactive than monohalide.

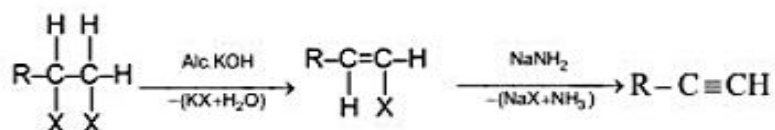
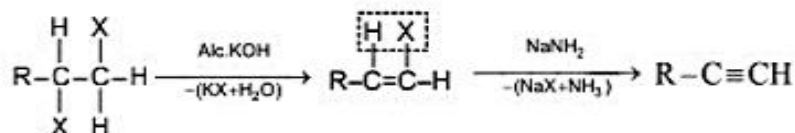
## CHEMICAL PROPERTIES OF DIHALIDES

- (a) Reaction with aqueous KOH : –



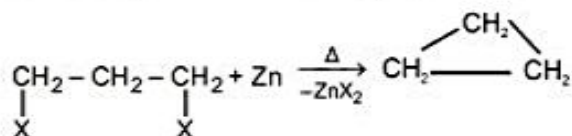


(b) Reaction with alcoholic KOH : –

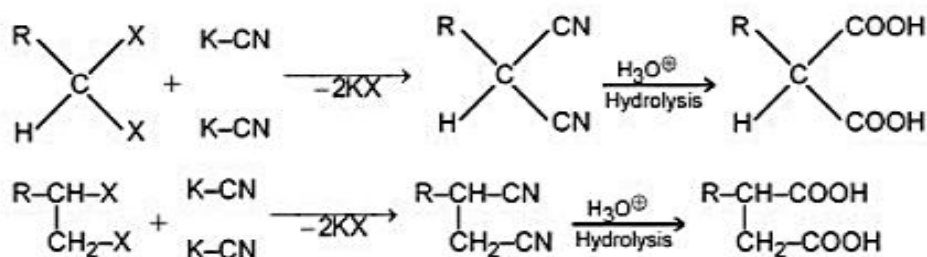


(c) **Reaction with zinc dust :** Gem dihalide reacts with Zn dust to form higher symmetrical alkene while vicinal dihalide reacts with Zn dust to form respective alkene.

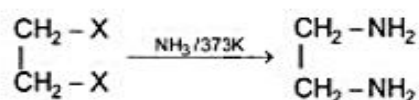
**Note** –  $\alpha$ ,  $\omega$  dihalide form cyclic alkane.



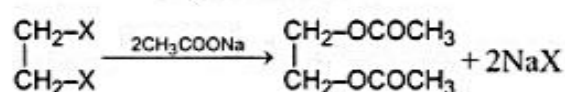
(d) Reaction with KCN :



(e) Other substitution reaction : –



ethylene amine

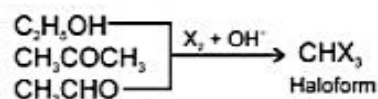


## TRIHALIDES

Trihalo derivatives of alkanes are known as trihalides. Reaction of method of preparation of trihalides is known as haloform reaction.

### TRIHALOALKANES : HALOFORM : $\text{CHX}_3$

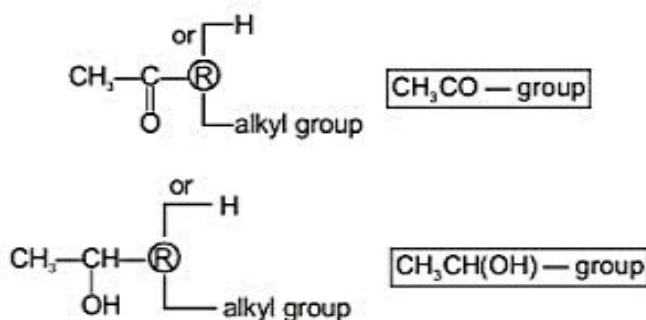
#### Preparation of Haloform



\* The following compound give haloform reaction.

\* Acetaldehyde, all methyl ketones, acetone, ethylalcohol, all 2-alkanols etc.

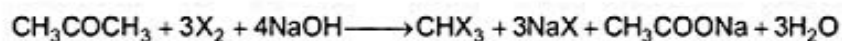
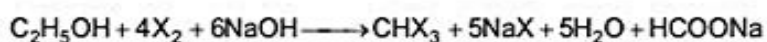
When the following compounds are heated with alkali and halogen haloform is obtained.



#### Example of methyl ketone :

- (i) Acetone ( $\text{CH}_3-\text{CO}-\text{CH}_3$ )
- (ii) Butanone ( $\text{CH}_3-\text{CO}-\text{CH}_2-\text{CH}_3$ )
- (iii) 2-Pentanone ( $\text{CH}_3-\text{CO}-\text{CH}_2-\text{CH}_2-\text{CH}_3$ )
- (iv) 3-Methylbutanone ( $\text{CH}_3-\text{CO}-\text{CH}(\text{CH}_3)_2$ )

#### Haloform Reaction



#### (i) Chloroform : $\text{CHCl}_3$

##### Preparation of Chloroform

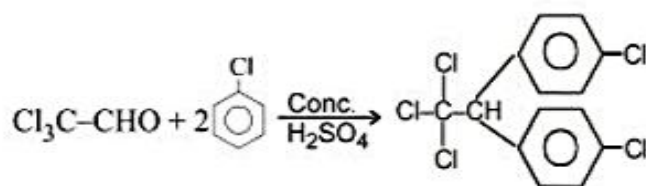
##### 1. Laboratory Methods – Chloroform Reaction

On heating ethyl alcohol with bleaching powder, the reaction occurs in the followings steps :

- (i)  $\text{CaOCl}_2 + \text{H}_2\text{O} \rightarrow \text{Ca}(\text{OH})_2 + 2\text{Cl}$
- (ii)  $\text{CH}_3\text{CH}_2\text{OH} + 2\text{Cl} \rightarrow \text{CH}_3\text{CHO} + 2\text{HCl}$
- (iii)  $\text{CH}_3\text{CHO} + 6\text{Cl} \rightarrow \underset{\text{Chloral}}{\text{CCl}_3\text{CHO}} + 3\text{HCl}$
- (iv)  $2\text{CCl}_3\text{CHO} + \text{Ca}(\text{OH})_2 \rightarrow 2\text{CHCl}_3 + (\text{HCOO})_2\text{Ca}$

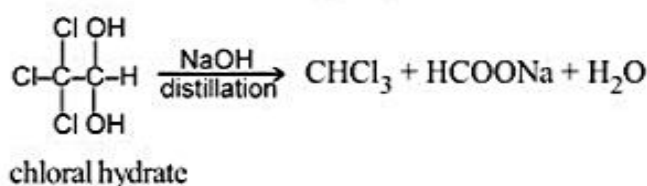


**Note :** (i) Chloral is an important compound and when it reacts with chlorobenzene in presence of conc.  $\text{H}_2\text{SO}_4$ , then it form an important compound DDT (Dichloro Diphenyl Trichloro ethane )

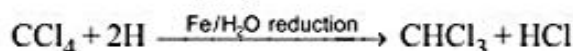


DDT [1,1,1-trichloro-2,2-bis (parachloro phenyl) ethane]

(ii) Preparation of pure Chloroform – Alkaline solution of chlorohydrate is used in the formation of chloroform. Which on distillation gives pure chloroform as follows :



**Preparation of trihalide using ‘Pyrene’ :**

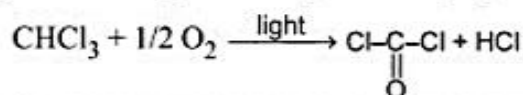


## PHYSICAL PROPERTIES

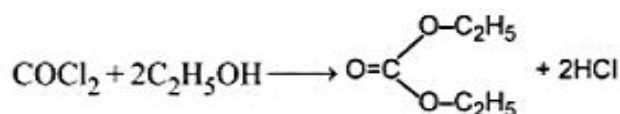
- Chloroform is colourless with pleasant smell.
- Insoluble in water and soluble in organic solvent. Vapours of chloroform are poisonous in nature.
- It cause temporary unconsciousness, so used as an anaesthetic agent.
- Boiling point of  $\text{CHCl}_3$  is  $61^\circ\text{C}$ .
- It is best solvent for fats, oil and wax.
- Iodoform is yellow crystalline solid. It has melting point  $119^\circ\text{C}$ .

## CHEMICAL PROPERTIES

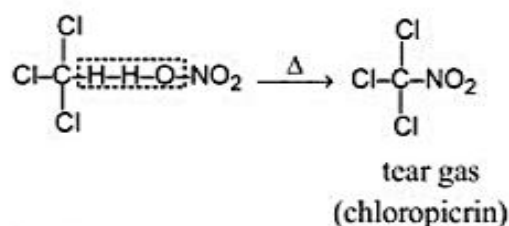
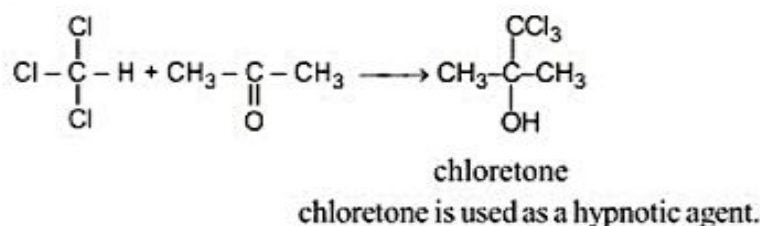
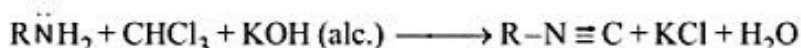
**Oxidation :** In presence of light it forms poisonous gas phosgene with atmospheric oxygen or with air.



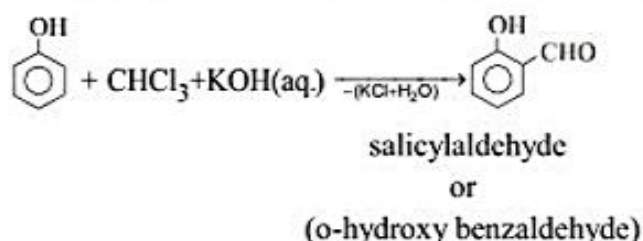
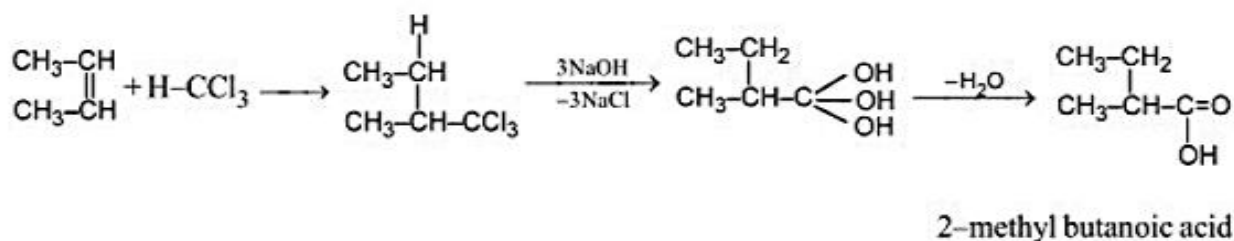
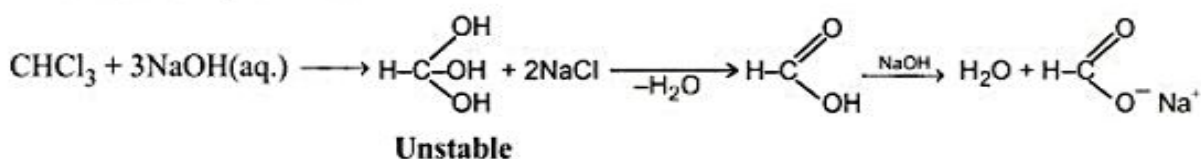
For protection it is kept into dark room in coloured bottle filling completely. For removal of phosgene we can use 0.5 to 1% ethanol solution which converts poisonous phosgene into non-poisonous salt diethyl carbonate.

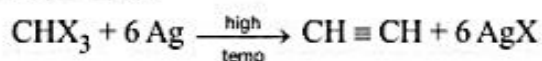
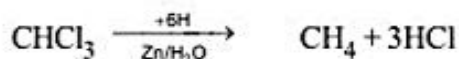
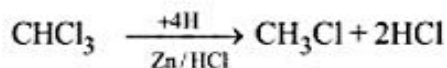
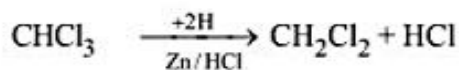


**Note :** We use silver nitrate solution to check the impurity of phosgene in solution which will form white ppt. of  $\text{AgCl}$  with  $\text{HCl}$

**Reaction with  $\text{HNO}_3$  :****Reaction with Acetone :****Reaction with Primary amine :**

The reaction is called as 'Hoffman-carbylamine Reaction' or 'Isocyanide-test'. These isocyanides (product) has offensive smell. So, the reaction is used to test 1° amine. Reacting species of reaction is dichloro carbene.

**Reaction with Phenol :** The reaction is called as 'Reimer-tiemann Formylation'.**Reaction with 2- Butene :****Reaction with aq. NaOH :**

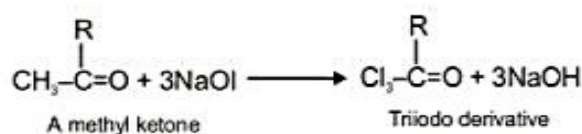
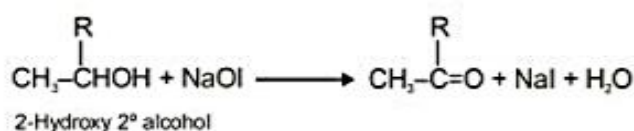
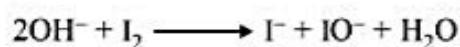
**Reaction with silver powder****(Dehalogenation) :****Reduction :****Uses**

1. As an anaesthetic
2. As a solvent for fat, oil and non-polar substances
3. As an antiseptic
4. In the manufacture of a hypnotic drug named chloretone
5. In the manufacture of a war gas named chloropicrin
6. In the manufacture of triphenylmethane dyes
7. In the manufacture of a polymer named teflon

**iodoform  $\text{CHI}_3$** **Iodoform Reaction**

A yellow precipitate of  $\text{CHI}_3$  is obtained on mixing saturated solution of sodium carbonate in the compound that gives haloform reaction, and heating the solution with adding iodine pinch by pinch. This reaction is called **iodoform test**.

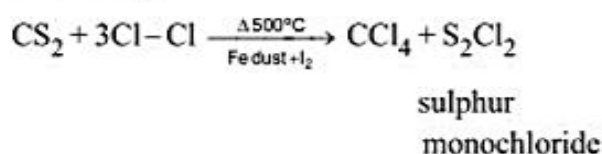
$\text{Na}_2\text{CO}_3$  is a strong base due to hydrolysis of  $\text{CO}_3^{2-}$  ion.



## TETRAHALIDE 'PYRENE'

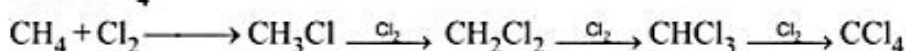
**General method of preparation :**

**From CS<sub>2</sub> :-**



The reaction is used for industrial production of CCl<sub>4</sub>.

**From CH<sub>4</sub> :**



**From CHCl<sub>3</sub> :**

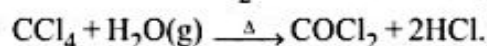


**Physical Properties :**

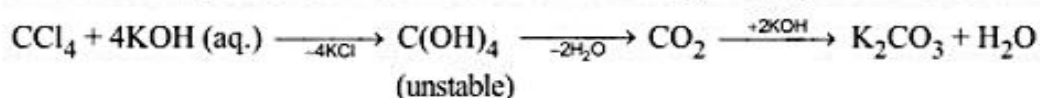
- It is colourless liquid with specific smell. It is insoluble in water and soluble in organic solvent.
- It is the only organic solvent which is non-combustible. So used as fire-extinguisher called as 'Pyrene'.

**Chemical Properties :**

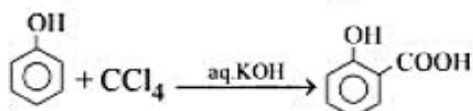
- It reacts with hot H<sub>2</sub>O or with water vapour and forms poisonous gas 'Phosgene'.



- It reacts with aqueous or alcoholic KOH and forms inorganic salt potassium carbonate.

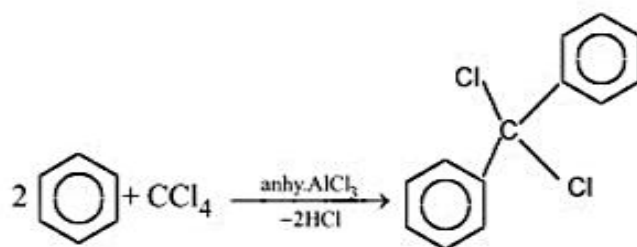


- It reacts with phenol and forms salicylic acid.



The reaction is called as 'Riemer-Tiemann Carboxylation'.

- Reaction with benzene.



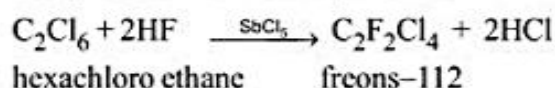
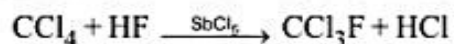
dichloro diphenyl methane



## FREONS

These are poly chlorofluoro derivative of alkane.

**Preparation of freons :**



**Nomenclature of Freons :**

The common name of freons is Freon - cba or freon C - 1, H + 1, F, where  
 c = no. of carbon atom - 1, b = no. hydrogen atom + 1, a = total no. of atoms of fluorine  
 eg.  $\text{CFCl}_3$                                   C - 1 = 0, H + 1 = 1, F = 3    Freon - 11

Formula	C-1	H + 1	F	Name
$\text{CFCl}_3$	$1 - 1 = 0$	$0 + 1 = 1$	1	Freon-11
$\text{CF}_2\text{Cl}_2$	$1 - 1 = 0$	$0 + 1 = 1$	2	Freon-12
$\text{C}_2\text{F}_2\text{Cl}_4$	$2 - 1 = 1$	$0 + 1 = 1$	2	Freon-112
$\text{C}_2\text{F}_3\text{Cl}_3$	$2 - 1 = 1$	$0 + 1 = 1$	3	Freon-113
$\text{C}_2\text{F}_4\text{Cl}_2$	$2 - 1 = 1$	$0 + 1 = 1$	4	Freon-114
$\text{C}_2\text{F}_5\text{Cl}$	$2 - 1 = 1$	$0 + 1 = 1$	5	Freon-115

**Properties & uses of freons : –**

- Freons are colourless, odourless, unreactive & non-combustible liquids.
- Having very low boiling points (e.g  $\text{CF}_2\text{Cl}_2 = -29.8^\circ\text{C}$ ). They easily converted from gaseous state to liquid state, therefore they are used as a coolant in A.C. & Refrigerator.
- Used as a aerosole propellant in aeroplane & rockets.
- Also used as a solvent.

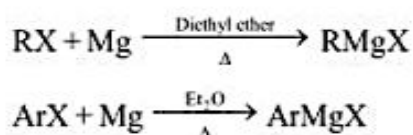
**Note :** CFC is the main cause of Ozone layer decay (CFC – chlorofluoro carbon)

## GRIGNARD REAGENTS

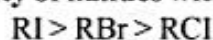
Organomagnesium halides were discovered by French chemist Victor Grignard in 1900.

### PREPARATION OF GRIGNARD REAGENTS

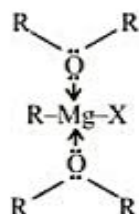
GR. are prepared by the reaction of organic halide (RX) with Mg in dry ether solvent.



The order of reactivity of halides with Mg is :



GR. form a complex with ether solvent and formation of this complex imparts stability to GR.



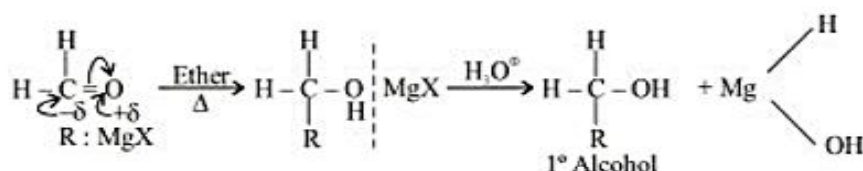
The method (which can be used for 1°, 2° and 3° alcohols) is little used in practice, since an alkyl halide can be converted into the corresponding alcohols.

### REACTIONS OF GRIGNARD REAGENTS

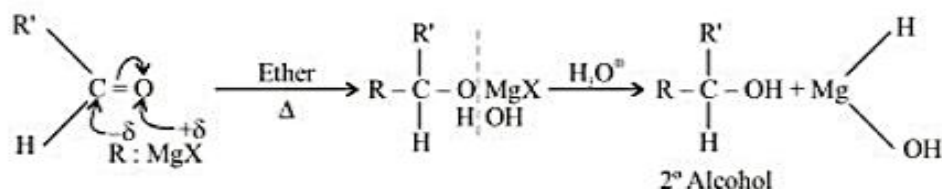
#### 1. Reaction with carbonyl compounds :

GR react with carbonyl compounds to give 1°, 2° and 3° alcohols.

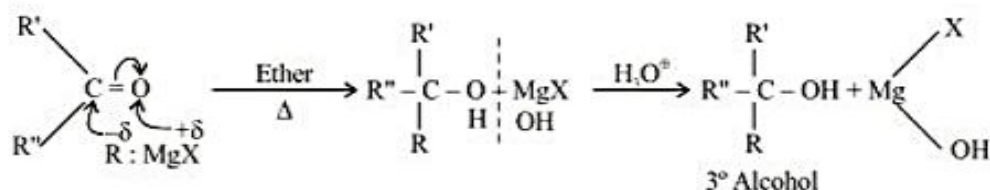
(a) GR. react with formaldehyde (methanal, HCHO) to gives 1° alcohol.



(b) GR. react with all other aldehydes to given 2° alcohols.

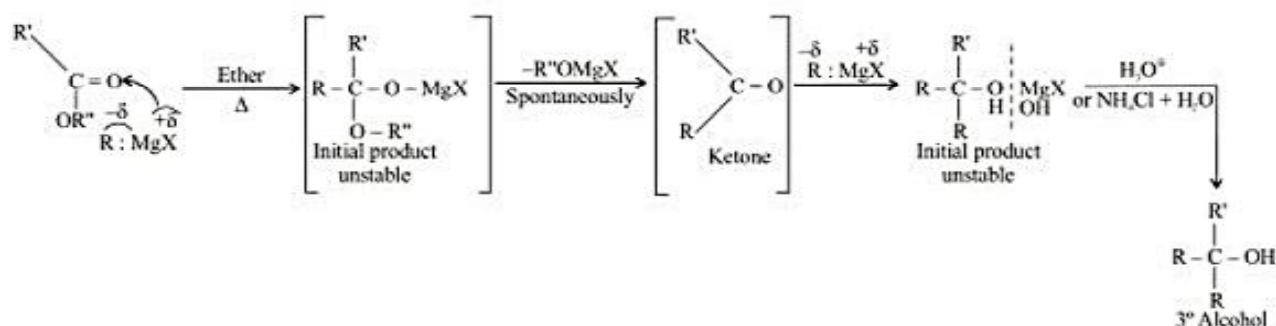


(c) G.R. react with ketones to give 3° alcohols.

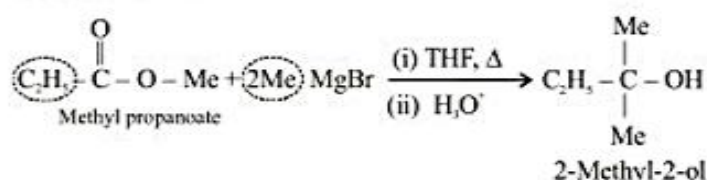


## 2. Reaction with ester :

Two moles of G.R. reacts with esters to give 3° alcohols. One mole of G.R. reacts with esters to form ketones. Ketones are more reactive towards G.R. than esters. Therefore, as soon as a molecule of the ketone is formed in the mixture, it reacts with a second molecule of G.R. After hydrolysis, the product is 3° alcohol, with two same alkyl groups that correspond to the alkyl portion of the G.R.



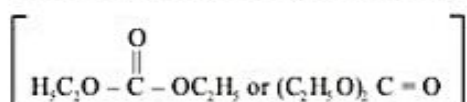
For example :



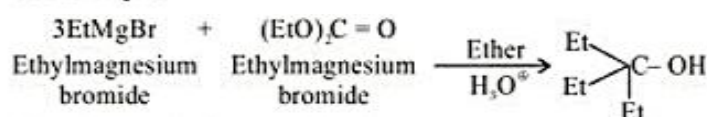
## 3. Reaction with dialkyl carbonate :

Preparation of 3° alcohol containing three identical alkyl groups :

This may be prepared by the reaction between 3 mol of G.R. with 1 mol of diethyl carbonate .



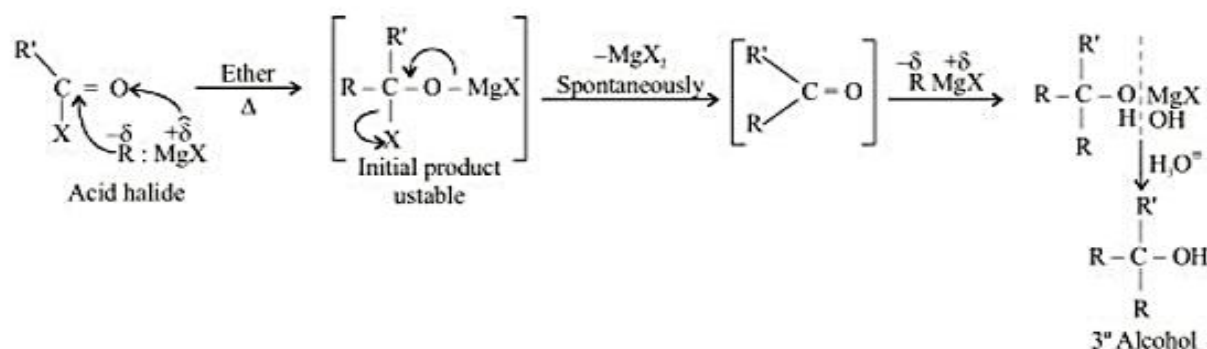
For example



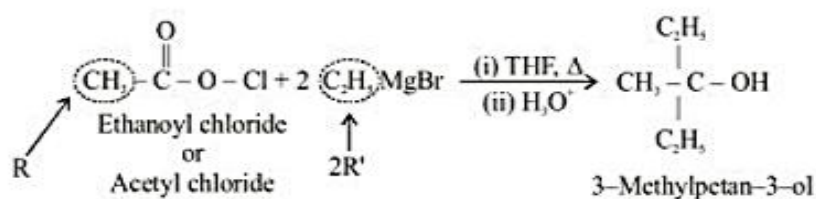
## 4. Reaction with alkanoyl halide :



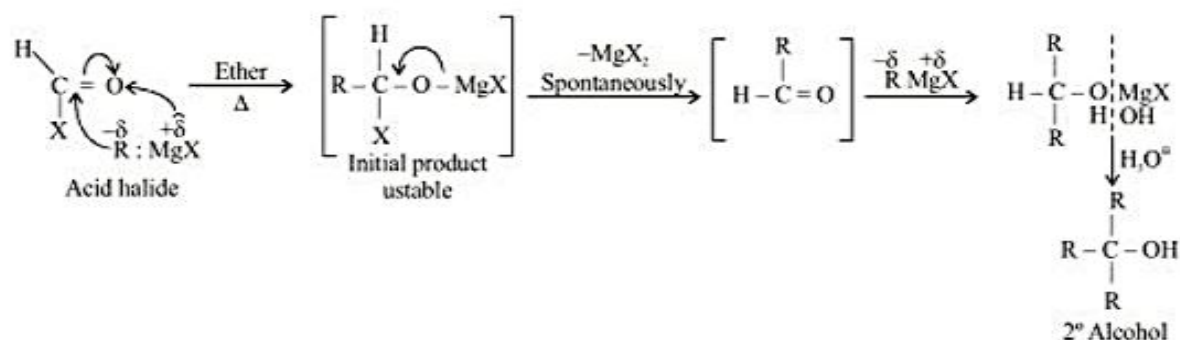
One mole of G.R. reacts with acid halides  $\left( \begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{X} \end{array} \right)$  to form ketones. Ketones are more reactive than acid halides. Therefore, as soon as a molecule of ketone is formed in the mixture, it reacts with a second molecule of G.R. After hydrolysis, the product is 3° alcohol, with two same alkyl groups that correspond to the alkyl portion of the G.R.



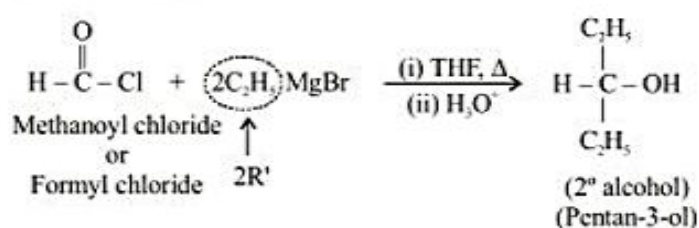
**For example :**



Two moles of G.R. reacts with formyl halides or methanoyl halides  $\left( \begin{array}{c} \text{O} \\ \parallel \\ \text{H}-\text{C}-\text{X} \end{array} \right)$  to give 2° alcohols, with two same alkyl groups that corresponds to the alkyl portion of the G.R.



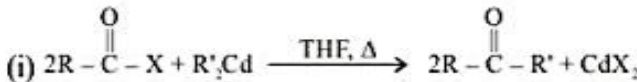
**For example :**





Reaction of dialkyl cadmium ( $R_2Cd$ ) or dialkyl lithium cuprate with acid halides  $\left( \begin{array}{c} O \\ || \\ R-C-X \end{array} \right)$  gives

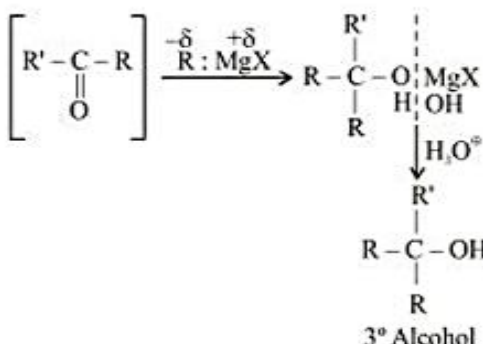
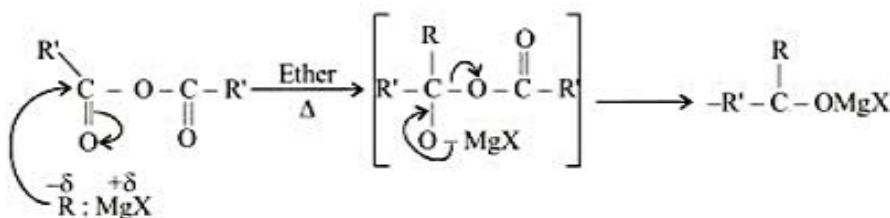
ketones and with formyl halides  $\left( \begin{array}{c} \text{O} \\ \parallel \\ \text{H}-\text{C}-\text{X} \end{array} \right)$  gives aldehydes.



**5. Reaction with anhydride :**

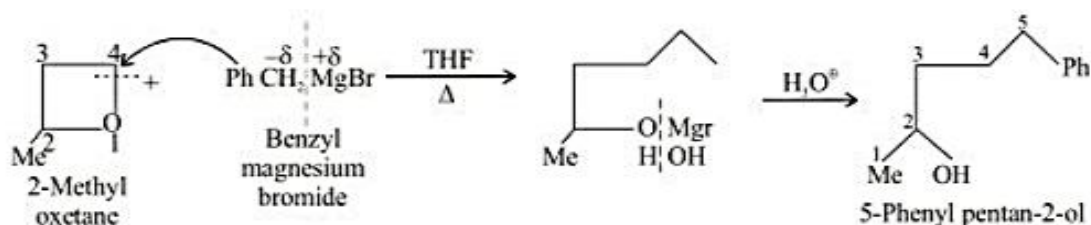
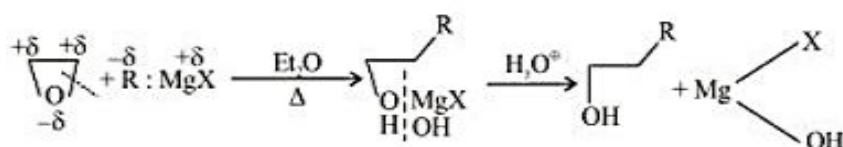
Two moles of G.R. reacts with acid anhydride  $\left( \text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{R} \right)$  to give 3° alcohol.

Acid anhydrides react in the same way as ester, and acid halides react with  $\text{RMgX}$ .



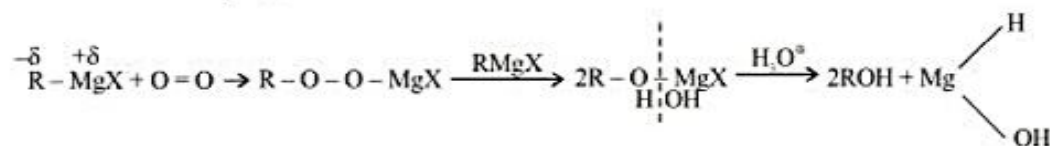
**6. Reaction of RMgX (G.R.) with oxirans (epoxides) and other cyclic ethers :**

RMgX reacts with oxiranes or cyclic ethers via  $S_N2$  mechanism. The  $R^-$  (nucleophile) of RMgX attacks the partially charged C atom of oxirane ring. Since it is highly strained, the ring opens and forms a salt of  $1^\circ$ C alcohol, which gives alcohol on acidification.

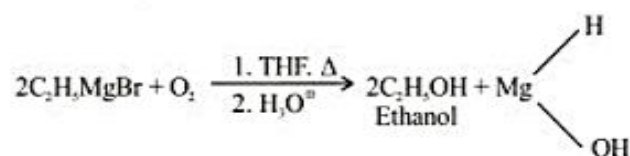


## 7. Reaction with O<sub>2</sub> :

G.R. react with O<sub>2</sub> to give 1° alcohol

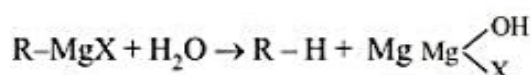
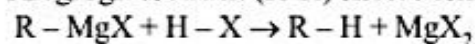


For example :



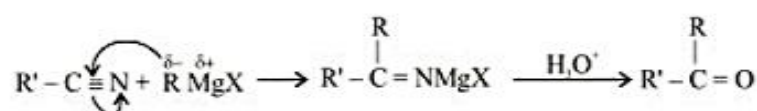
## 8. Reaction with acids :

RMgX gives alkane (R-H) on reaction with acids

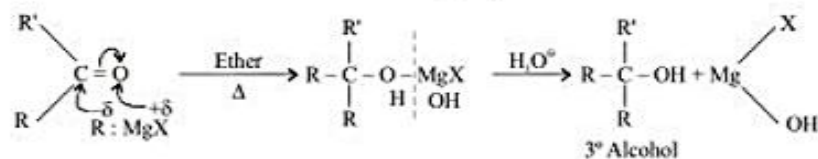


## 9. Reaction with R-CN :

RMgX gives ketone on reaction with R-CN



Ketone on further reaction with RMgX gives 3° alcohol.



## **CO-ORDINATION COMPOUNDS**

### **INTRODUCTION**

- (a) The concept of coordination compounds arises from the complex formation tendency of transition elements.
- (b) These compounds play a vital role in our life. Haemoglobin of animal blood and chlorophyll of plants are also coordination compounds of Fe and Mg respectively.

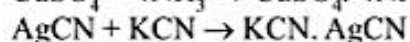
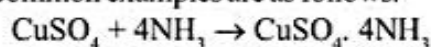
### **COMPLEX FORMATION**

- Transition metal ions have maximum tendency to form complexes. In the formation of complexes they form coordinate covalent bonds and act as electron pair acceptors.
- Transition metal ions have smaller size and have high positive charge i.e., high charge density. Due to this they have maximum tendency to accept electrons. They have vacant 'd' orbitals available on them hence they can accept lone pairs of electrons forming coordinate covalent bond.
- The greater the charge density on the transition metal ion, the greater they have tendency to form complexes. Thus  $Ti^{+2}$  to  $Ni^{+2}$  the stability of complexes formed goes on increasing.
- Compounds like NaCl,  $Al_2(SO_4)_3$  and  $K_2SO_4$  provide only two types of ions in aqueous solution i.e., cations and anions, are called as simple salts.
- When two or more simple salt solutions are mixed and then subjected for crystallisation, the crystals which are obtained are of addition compounds.

### **MOLECULAR OR ADDITION COMPOUNDS**

- (a) When solutions containing two or more simple stable compounds in molecular proportions are allowed to evaporate, crystals of new substances are obtained. These substances are termed molecular or addition compounds.

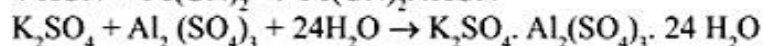
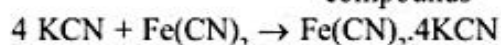
- (b) Some common examples are as follows.



simple stable      Addition or

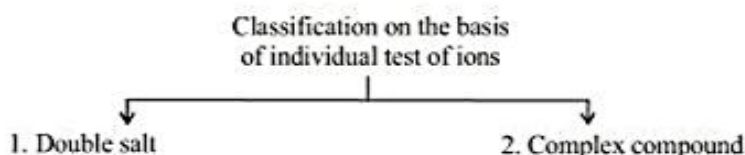
compounds      molecular

compounds



Alum

- (c) The molecular or addition compounds are of two types : Double salts or lattice compound and coordination or complex compound





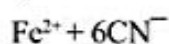
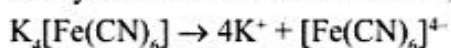
**1. Double salts or lattice compounds**

- (a) The addition compounds which are stable in solid state only but are broken down into individual constituents when dissolved in water are called double salts or lattice compounds.
- (b) Their solutions have the same properties as the mixture of individual compounds
- (c) For example when carnallite ( $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ) is dissolved in water it exhibits the properties of  $\text{KCl}$  and  $\text{MgCl}_2$

**2. Coordination or complex compounds**

- (a) The addition compounds in which some of the constituent ions or molecules lose their identity and when dissolved in water they do not break up completely into individual ions are called coordination compounds
- (b) The properties of their solutions are different than those of their constituents.
- (c) In such compounds there is complex ion which is a central metal ion with lewis bases attached to it through coordinate covalent bonds.
- (d) On the basis of stability of complex ion, complex ions are further divided as follows.

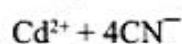
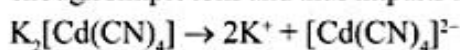
(i) Perfect complexes : Those in which complex ion is fairly stable and is either not dissociated or feebly dissociated in solution state, e.g.



(feebly dissociated)

The ferrocyanide ion  $[\text{Fe}(\text{CN})_6]^{4-}$  is so insignificantly dissociated that it can be considered as practically undissociated and does not give the test of  $\text{Fe}^{2+}$  or  $\text{CN}^-$  ions

(ii) Imperfect complexes : Those in which complex ion is less stable and is reversibly dissociated to give enough simple ions and thus imparts their tests, e.g.



(appreciably dissociated)

**Note :** An imperfect complex may be too unstable to exist and may be completely dissociated in solution, it then becomes a double salts

**Illustration**

1. Study the following double salt and write the type of ions which can be tested in their aqueous solution.

**Salt****Ions can be tested**

- (a)  $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$   
 (b)  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$   
 (c)  $\text{K}_2\text{SO}_4 \cdot \text{Cr}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$   
 (d)  $\text{FeSO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$   
 (e)  $\text{Al}_2(\text{OH})_3\text{PO}_4 \cdot \text{H}_2\text{O}$

**Sol.****Salt****Ions can be tested**

- (a)  $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$   
 (b)  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$   
 (c)  $\text{K}_2\text{SO}_4 \cdot \text{Cr}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$   
 (d)  $\text{FeSO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$   
 (e)  $\text{Al}_2(\text{OH})_3\text{PO}_4 \cdot \text{H}_2\text{O}$

$\text{K}^+, \text{Al}^{3+}, \text{SO}_4^{2-}$   
 $\text{NH}_4^+, \text{Al}^{3+}, \text{SO}_4^{2-}$   
 $\text{K}^+, \text{Cr}^{3+}, \text{SO}_4^{2-}$   
 $\text{Fe}^{2+}, \text{Al}^{3+}, \text{SO}_4^{2-}$   
 $\text{Al}^{3+}, \text{OH}^-, \text{PO}_4^{3-}$

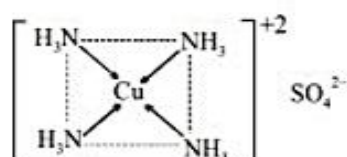


### Exercise

1. Predict which among the following properties given below belong to double salt and co-ordination compounds.
- The blue coloured solution prepared by  $\text{Cu}^{+2}(\text{aq.})$  and  $\text{NH}_3(\text{NH}_4^+ \text{aq.})$  does not show the presence of  $\text{Cu}^{+2}$  (.....)
  - Compounds which are stable in the solid state but break up into its constituents in aqueous solution (.....)
  - Aq. solution of carnallite (.....)
  - The Compounds in which central metal ion form dative bonds with species surrounding it. (.....)
  - Mohrs salt (.....)
- Sol. (a) Co-ordination (b) Double salt (c) Double salt (d) Co-ordination (e) Double salt

### VARIOUS TERMS USED IN CO-ORDINATION COMPOUNDS

- Complex ion :** An aggregate of metal ion with anions cation or neutral molecules is called as complex ion. The metal ion which forms complex ion in combination with anions or neutral molecules is called as central metal ion. Central metal ion acts as an electron pair acceptor and forms coordinate covalent bond. The anions or neutral molecules which combine with central metal ion to form complex ion are called as ligands. They act as electron pair donors or Lewis bases.
- Central metal ion :**
  - The metal ion which forms complex ion in combination with anions or neutral molecules is called as **central metal ion**.
  - Central metal ion acts as an electron pair acceptor and forms coordinate bond with ligands.
- Coordination Number :**
  - The number of atoms of the ligands that are directly bond to the central metal atom or ion by coordinate bonds is known as the coordination number of the metal atom or ion.
  - It is actually the number of coordinate covalent which the ligands form with the central metal atom or ion
  - Some common coordination numbers exhibited by metal ions are 2,4,6. The light transition metals exhibit 4 and 6 coordination numbers while heavy transition metals may exhibit coordination number more than 6
  - For example, the coordination number of Ni in the complex  $[\text{Ni}(\text{NH}_3)_4]\text{Cl}_2$  is 4 and that of Pt in the complex  $\text{K}_2[\text{PtCl}_6]$  is 6
- Coordination sphere-(entity) :**
  - The central metal atom and the ligands directly attached to it are collectively termed as the coordination sphere.
  - Coordination sphere is written inside square bracket, for example  $[\text{Co}(\text{NH}_3)_6]^{3+}$
  - The part outside the bracket is called **ionisation sphere**.
  - The species present in the coordination sphere are nonionizable.
  - The species present in the ionization sphere are ionisable.



**(e) Oxidation state :**

- (i) It is number which represents the electric charge on the central metal atom of a complex ion.
- (ii) Example the oxidation number of Fe, Co and Ni in  $[\text{Fe}(\text{CN})_6]^{+}$ ,  $[\text{Co}(\text{NH}_3)_6]^{3+}$  and  $\text{Ni}(\text{CO})_4$  is +2, +3 and zero respectively.

**(f) Charge on the complex ion :**

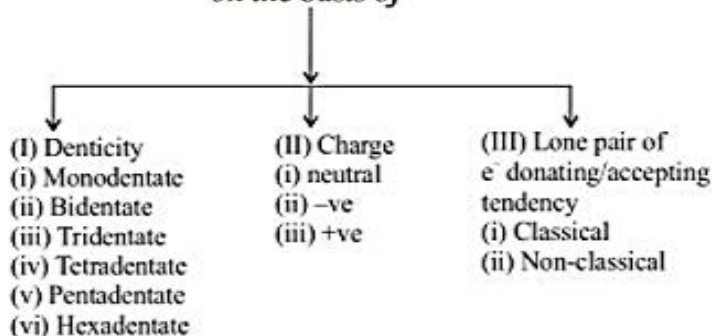
It is the algebraic sum of the total charge of the ligands and central metal ion.

Ex.  $\text{K}_4[\text{Fe}(\text{CN})_6]$  total charge on the complex ion is  $-4$ .

**(g) Ligands :**

- (i) The anions or neutral molecules which combine with central metal ion to form complex ion are called as ligands.
- (ii) They act as electron pair donor or Lewis bases, but strong crystal field ligands like CO, CN<sup>-</sup> etc. can also accept electron pair from the metal ion, because these ligands are  $\pi$ -acids ligands.

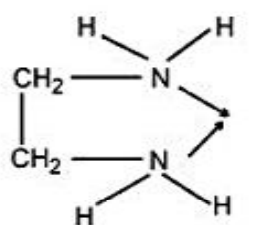
**Classification of the Ligand  
on the basis of**

**(I) CLASSIFICATION ON THE BASIS OF DENTICITY**

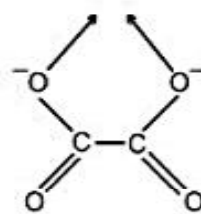
- (i) **Mono-or unidentate ligands :** They have one donor atom, i.e. they supply only one electron pair to central metal atom or ion.

Examples :  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{CN}^-$ ,  $\text{NO}_2^-$ ,  $\text{OH}^-$ , CO, Py,  $\text{H}^-$

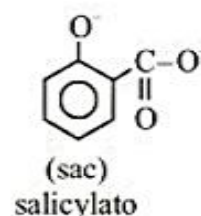
- (ii) **Bidentate ligands :** Ligands which have two donor atoms and have the ability to link with central metal ion at two positions are called bidentate ligands. Some examples are :



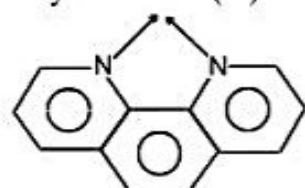
Ethylenediamine (en)



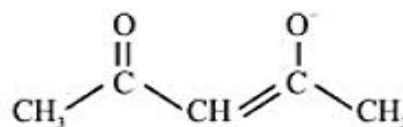
Oxalate (ox)



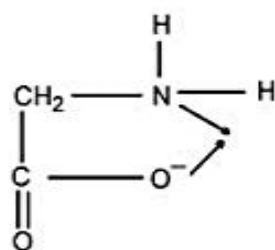
(sac)  
salicylato



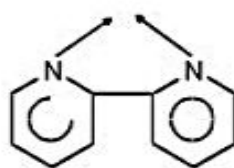
1,10-Phenanthroline (o-phen)



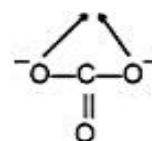
(acac)  
acetylacetonato



Glycinato (Gly)

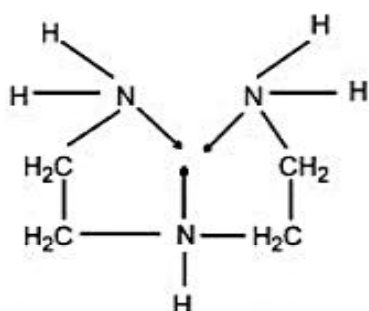


2,2'-Dipyridyl (Dipy)

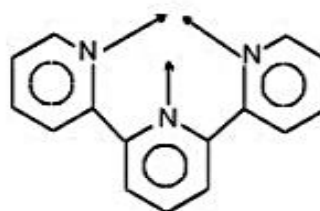


Carbonato

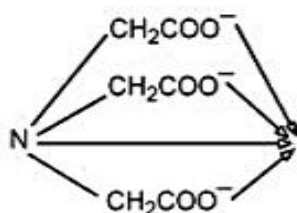
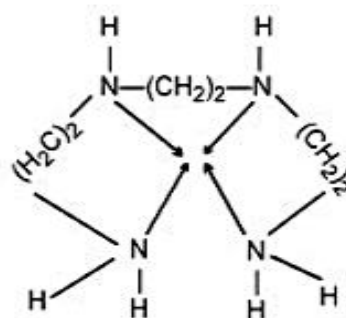
(iii) **Tridentate ligands** : The ligands having three donor atoms are called tridentate ligands. Examples are:



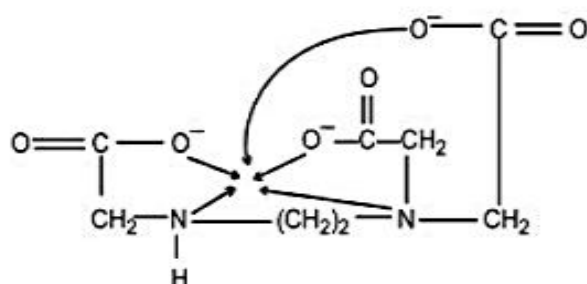
Diethylene triamine (Dien)

2,2',2''-Terpyridine  
(terpy)

(iv) **Tetradentate ligands** : These ligands possess four donor atoms. Examples are:

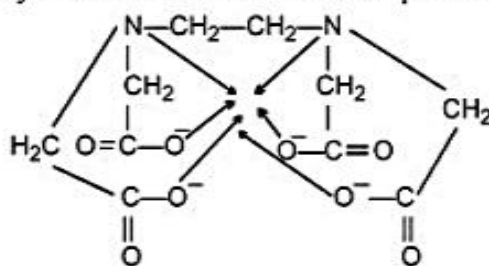
(Nitrilotriacetato)  
(NTA)Triethylene tetramine  
(Trien)

(v) **Pentadentate ligands** : They have five donor atoms. For example, ethylenediamine triacetate ion.

Ethylenediamine triacetato ion (EDTA)<sup>3-</sup>



- (vi) **Hexadentate ligands:** They have six donor atoms. The most important example is ethylenediamine tetraacetate ion.



Ethylenediamine tetraacetate ion (EDTA)<sup>4-</sup>

### Classification of ligands on the basis of donor and acceptor properties of the ligands

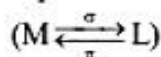
#### (A) Ligands having one (or more) lone pair (or pairs) of electrons

- (a) Ligands which contain vacant  $\pi$ -type orbitals that can receive back donated  $\pi$  electron from metal ion in low oxidation state.

e.g.: CO, NO,  $\text{CN}^-$ ,  $\text{NC}^-$ ,  $\text{R}-\text{N} \equiv \text{C}$ ,  $\text{R}_3\text{P}$ ,  $\text{R}_3\text{As}$

$\alpha, \alpha$ -dipyridyl, o-phenanthroline

- (b) All these ligands also have filled donor orbital in addition to vacant  $\pi$ -type acceptor orbitals.  
(c) Thus in these complexes both metal and ligand function as donors and acceptors



- (d) Ligands which do not have vacant orbitals to receive back donated electron from metals  
e.g.  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{F}^-$ .

#### (B) Ligands having no lone pairs of electrons but have $\pi$ bonding electron

e.g. Ethylene, benzene, cyclopentadienyl-ion

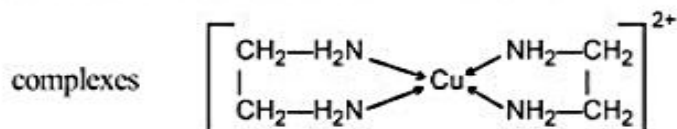
$\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)]$  Zises salt

### SPECIAL LIGAND

- (1) **Polydentate ligands:** have Flexidentate character, it is not necessary that all the donor atoms present in the polydentate ligands should form coordinate bonds with central metal atom or ion.
- (2) **Ambidentate Ligand:** Ligands which can ligate through two different atoms present in it are called ambidentate ligands. Examples of such ligands are the  $\text{NO}_2^-$  and  $\text{SCN}^-$  ions.  $\text{NO}_2^-$  ion can coordinate through either the nitrogen or the oxygen atoms to a central metal atom/ion. Similarly,  $\text{SCN}^-$  ion can coordinate through the sulphur or nitrogen atom. Such possibilities give rise to linkage isomerism in coordination compounds. There are certain ligands which have two or more donor atoms but during formation of complexes only one donor atom is attached to metal ion. Such ligands are called **ambidentate ligands** such as  $\text{CN}^-$ ,  $\text{CNS}^-$ .
- (3) **Chelating ligands.**
  - (a) Polydentate ligands whose structures permit the attachment of two or more donor sites to the same metal ion simultaneously, thus closing one or more rings are called chelating ligands and the compounds formed are known as chelate compounds.
  - (b) A chelate may be defined as a ring structure formed by the combination of a polydentate ligand having two or more donor atoms with a metal ion forming part of the ring.



- (c) The process of formation of chelates is called chelation.  
 (d) Chelate complexes are more stable than ordinary complexes in which the ligand is a monodentate  
 (e) This increased stability of the compound due to chelation is called the chelate effect  
 (f) In the complex ion given below, 5 membered rings are formed. So all these are called chelate



- (g) Generally the chelate complexes with 5 or 6 membered rings are more stable.  
 (h) Out of these, 5 membered rings are very stable when they involve saturated ligands.  
 (i) On the other hand 6-membered ring structures acquire maximum stability when they involve unsaturated ligands containing conjugate double bond. This is due to the resonance effects involving metal d-orbitals and ligand p-orbital electrons.

### Illustration

1. Match the Column.

A	B
(i) Ligand contains one donor site	(a) hexadentate
(ii) Ligand contains two donor site	(b) tridentate
(iii) Ligand contain three donor site	(c) tetradentate
(iv) Ligand contain four donor site	(d) bidentate
(v) Ligand contain six donor site	(e) unidentate

Sol. (i) - (e); (ii) - (d); (iii) - (b); (iv) - (c); (v) - (a)

### Exercise

1. In the coordination compound,  $\text{K}_4[\text{Ni}(\text{CN})_4]$ , the oxidation state of nickel is :  
 (A) -1 (B) 0 (C) +1 (D) +2

Ans. (B)

2. Which of the following species is not expected to be a ligand  
 (A)  $\text{NO}^+$  (B)  $\text{NH}_4^+$  (C)  $\text{NH}_2-\text{NH}_3^+$  (D) CO

Ans. (B)

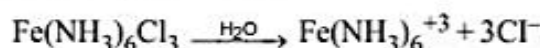
## WERNER'S COORDINATION THEORY

Alfred Werner (considered as the father of coordination chemistry) studied the structure of coordination complexes such as  $\text{CoCl}_3 \cdot 6\text{NH}_3$  and  $\text{CuSO}_4 \cdot 4\text{NH}_3$  in 1893.

According to him :

- (a) Each metal in coordination compound possesses two types of valencies :  
 (i) primary valency or principal valencies or ionisable valencies.  
 (ii) Secondary valency or nonionisable valencies  
 (b) Primary valencies are satisfied by anions only. The number of primary valencies depends upon the oxidation state of the central metal. It may change from one compound to other. These are represented by dotted lines between central metal atom and anion.

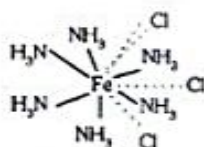
- (c) Secondary valencies are satisfied only by electron pair donor, the ions or the neutral species. These are represented by thick lines.
- (d) Each metal has a fixed number of secondary valencies, also referred to as coordination number. The coordination number depends mainly on the size and the charge on the central atom. The maximum number of ions or molecules that the central atom can hold by secondary valencies is known as coordination number.
- (e) The ions attached to primary valencies possess ionising nature whereas the ions attached to secondary valencies do not ionise when the complex is dissolved in a solvent.
- (f) Every central ion tends to satisfy its primary as well as secondary valencies.
- (g) The secondary valencies are directional and are directed in space about the central metal ion. The primary valencies are non-directional. The presence of secondary valencies gives rise to stereoisomerism in complexes.
- (h) Initially, Werner had pointed out coordination number of a metal atom to be four or six.
- (i) The six valencies were regarded to be directed to the corners of a regular octahedron circumscribed about the metal ion. For metals having four coordination number, the four valencies are either arranged in a planar or tetrahedral nature.
- (j)  $\text{Fe}(\text{NH}_3)_6\text{Cl}_3$  forms 3 moles of  $\text{AgCl}$  in the form of precipitate on addition of  $\text{AgNO}_3$  solution. This indicates that the complex ionises as



- (i) Electrical conductance of complexes - More the number of ions provided greater is the electrical conductance of the complex in aqueous medium.

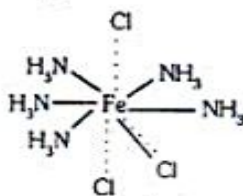
e.g. - The electrical conductance of aqueous  $\text{Fe}(\text{NH}_3)_6\text{Cl}_3$  is greater than that of aqueous solution of  $[\text{Fe}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ .  $[\text{Fe}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2 \rightarrow [\text{Fe}(\text{NH}_3)_5\text{Cl}]^{+2} + 2\text{Cl}^-$  Total 3 ions

Representation of complexes - Werner's representation for  $\text{Fe}(\text{NH}_3)_6\text{Cl}_3$

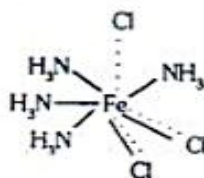


(Dotted lines indicate primary Valency and continuous lines indicate secondary valency of metal ion.) If the complex is

- (ii)  $\text{Fe}(\text{NH}_3)_5\text{Cl}_3$  Then in this complex 'Cl' groups act as primary valencies and one of the 'Cl' acts as secondary valency also. Thus werner's representation for this complex will be



- (iii)  $\text{Fe}(\text{NH}_3)_4\text{Cl}_3$  In this complex 'Cl' groups act as primary valencies and two of the 'Cl' group act as secondary valencies also. Thus this complex is represented as







Complex	Metal (Oxidation State)	Atomic Number of Metal	Coordination number	Effective atomic number (E.A.N.)
$K_4[Fe(CN)_6]$	+2	26	6	$(26-2) + (6 \times 2) = 36$ [Kr]
$[Cu(NH_3)_4]SO_4$	+2	29	4	$(29-2) + (4 \times 2) = 35$
$[Co(CH_3)_6]Cl_3$	+3	27	6	$(27-3) + (6 \times 2) = 36$ [Kr]
$Ni(CO)_4$	0	28	4	$(28-0) + (4 \times 2) = 36$ [Kr]
$K_2[Ni(CN)_4]$	+2	28	4	$(28-2) + (4 \times 2) = 34$
$K_2[PtCl_6]$	+4	78	6	$(78-2) + (6 \times 2) = 86$ [Rn]
$K_3[Cr(C_2O_4)_3]$	+3	24	6	$(24-3) + (6 \times 2) = 33$
$K_3[Fe(C_2O_4)_3]$	+3	26	6	$(26-3) + (6 \times 2) = 35$
$K_2[HgI_4]$	+2	80	4	$(80-2) + (4 \times 2) = 86$ [Rn]
$[Ag(NH_3)_2]Cl$	+1	47	2	$(47-1) + (2 \times 2) = 50$
$K_2[PdCl_4]$	+2	46	4	$(46-2) + (4 \times 2) = 52$

### Illustration

1. Calculate the EAN of the following complex.

Complex	Metal (Oxid. state)	At. No. of metal	Coordination number	Effective atomic number $EAN = (At. No. - O.N) + 2 \times$
$K_4[Fe(CN)_6] + 2$ $[Cu(NH_3)_4]SO_4$ $[Co(NH_3)_6]Cl_3$ $[Ni(CO)_4]$ $K_2[Ni(CN)_4]$ $K_2[PtCl_6]$ $K_3[Cr(C_2O_4)_3]$ $K_3[Fe(CN)_6]$ $K_2[HgI_4]$ $[Ag(NH_3)_2]Cl$	26		6	$(26 - 2) + (6 \times 2) = 36$ [Kr]

Sol. Calculate the EAN of the following complex.

Complex	Metal (Oxid. state)	At. No. of metal	Coordination number	Effective atomic number $EAN = (At. No. - O.N) + 2 \times$
$K_4[Fe(CN)_6]$	+2	26	6	$(26 - 2) + (6 \times 2) = 36$ [Kr]
$[Cu(NH_3)_4]SO_4$	+2	29	4	$(29 - 2) + 2 \times 4 = 35$ [Br]
$[Co(NH_3)_6]Cl_3$	+3	27	6	$(27 - 3) + 2 \times 6 = 36$ [Kr]
$[Ni(CO)_4]$	+4	28	4	$(28 - 4) + 2 \times 4 = 32$ [Ge]
$K_2[Ni(CN)_4]$	+2	28	4	$(28 - 2) + 2 \times 4 = 34$ (Se)
$K_2[PtCl_6]$	+4	78	6	$(78 - 4) + 2 \times 4 = 82$ [Pb]
$K_3[Cr(C_2O_4)_3]$	+3	24	3	$(24 - 3) + 2 \times 3 = 29$ [Cu]
$K_3[Fe(CN)_6]$	+3	26	6	$(26 - 3) + 2 \times 6 = 35$ [Br]
$K_2[HgI_4]$	+2	80	4	$(80 - 2) + 2 \times 4 = 84$ [Po]
$[Ag(NH_3)_2]Cl$	+1	47	2	$(47 - 1) + 2 \times 2 = 50$ [Sn]

### Exercise

1. In the complex  $Fe(CO)_x$ , the value of x is, if it follows sidwick EAN rule :

(A) 3

(B) 4

(C) 5

(D) 6

Ans. (C)



## I.U.P.A.C. NAMING OF COORDINATION COMPOUNDS

Due to wide variety of coordination compounds it is essential to use a unified system of nomenclature. Though a lot of compounds are known by their trivial names only, but I.U.P.A.C. has introduced rules for the naming of coordination compounds as follows :

### The order of listing the ions

- In common salts cation is named first and then the anion.
- In the complex ion (Cation or anion) ligands are named first followed by the name of central atom
- The oxidation state of the central metal is indicated by Roman numeral in brackets immediately after its name; (0) indicates zero oxidation state.
- In case the complex is non ionic, it is named as one word e.g.  $[\text{Ni}(\text{CO})_4]$  is called tetracarbonyl nickel (0)
- The suffix -ate is added to the name of central metal forming anionic complex ion. In cationic complex ion, the name of metal (usual name) is followed by the oxidation number in bracket. However in some metals Latin names are preferred in place of English names e.g. iron as ferrate, lead as plumbate and silver as argentate.

### Name of the ligand

- If there are two or more different kinds of ligands, they are named in alphabetical order without separation by hyphen.
- When there are several ligands of same kind, they are listed alphabetically

Symbol	Name as ligand	Symbol	Name as ligand
$\text{Cl}^-$	Chlorido	$\text{N}^{3-}$	Nitrido
$\text{Br}^-$	Bromo/Bromido	$\text{O}_2^{2-}$	Peroxo
$\text{CN}^-$	Cyanido	$\text{S}^{2-}$	Sulphido
$\text{O}^{2-}$	Oxido	$\text{NH}^{2-}$	imido
$\text{OH}^-$	Hydroxido	$\text{NH}_2^-$	amido
$\text{H}^-$	Hydridido	$\text{SO}_3^{2-}$	Sulphito
$\text{CO}_3^{2-}$	Carbonato	$\text{CH}_3\text{COO}^-$	Acetato
$\text{C}_2\text{O}_4^{2-}$	Oxalato	$\text{NO}_2^-$	(bonded through oxygen) nitrito (bonded through nitrogen) nitro
$\text{SO}_4^{2-}$	Sulphato		
$\text{NO}_3^-$	Nitrato		
$\text{S}_2\text{O}_3^{2-}$	Thiosulphato		

- Names of positive ligands ends in 'ium' e.g.  
 $\text{NO}^+$  Nitrosylium  
 $\text{NH}_2\text{NH}_3^+$  Hydrazinium
- If the number of a particular ligand is more than one in the complex ion, the number is indicated by using Greek numbers such as di, tri, tetra, penta, hexa, etc. However, when the name of the ligand includes a number, e.g. dipyridyl, ethylene diamine, then bis, tris, tetrakis are used in place of di, tri, tetra, etc
- In case of chelating ligands or ligands having di, tri, tetra, etc, in their name the prefixes bis, tris, tetrakis are used before ligands placed in parenthesis
- In poly nuclear complexes, the bridging group is indicated in the formula of the complex by separating it from the rest of complex by hyphens and adding before its name or in poly nuclear complex (a complex with two or more metal atoms) bridging ligands (which links two metal atoms) is denoted by the prefix  $\mu$  before its name.

S.No.	Complex Compounds	IUPAC Name
(i)	$K_4[Fe(CN)_6]$	Potassium hexacyanidoferrate (II)
(ii)	$K_2[PtCl_6]$	Potassium hexachloridoplatinate (IV)
(iii)	$[Co(NH_3)_6]Cl_3$	Hexammine cobalt (III) chloride
(iv)	$[Cr(H_2O)_4Cl_2]Cl$	Tetraaquadichloridochromium (III) chloride
(v)	$[Pt(NH_3)_2Cl_4]$	Diamminetetrachloridoplatinum (IV)
(vi)	$[Co(NH_3)_3Cl_3]$	Triamminetrichloridocobalt (III)
(vii)	$K_3[Co(NO_2)_6]$	Potassium hexanitridocobaltate (III)
(viii)	$Na_3[Fe(CN)_5NO]$	Sodium pentacyanido nitrosyl ferrate(II)
(ix)	$[NiCl_4]^{2-}$	Tetrachloridonickelate (II) ion
(x)	$[Ru(NH_3)_5Cl]^{+2}$	Pentamminechloridoruthenium (III) ion
(xi)	$[Fe(en)_3]Cl_3$	Tris(ethylenediamine) iron (III) chloride
(xii)	$[Ni(Gly)_2]$	Bis(glycinato)nickel (II)

### Illustration

1. Write the systematic names of the following coordination entities and compounds:  
 (i)  $[CoCl_2(NH_3)_4]^+$  (ii)  $[CrCl_3(NH_3)_3]$  (iii)  $K_3[Cr(C_2O_4)_3]$  (iv)  $K_4[Fe(CN)_6]$   
 (v)  $[PtCl(NH_3)_5]Cl_3$
- Sol. (i) tetraamminedichlorido Cobalt(III) (ii) triamminetrichloridochromium(III)  
 (iii) potassium trioxalatochromate(III) (iv) potassium hexacyanoferrate(II)  
 (v) pentaamminechloridoplatinum(IV) chloride

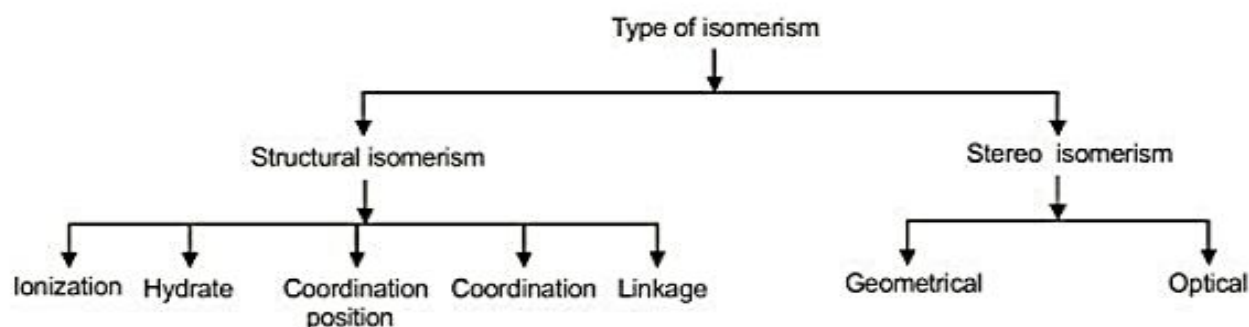
### Exercise

1. The IUPAC name  $[Co(NH_3)_6][Cr(CN)_6]$  is –  
 (A) Hexaammine cobalt (III) hexacyanochromate (III)  
 (B) Hexacyanochromium cobalt hexaammine (VI)  
 (C) Hexaammine cobalt (III) hexacyanochromium (VI)  
 (D) Hexacyanochromium (III) hexaammine cobalt (III)
- Ans. (A)
2. The IUPAC name for  $[Co(NCS)(NH_3)_5]Cl_2$  is –  
 (A) Pentaammine (thiocyanato-N) cobalt (III) chloride  
 (B) Pentaammine (thiocyanato-S) cobalt (III) chloride  
 (C) Pentaamine (isothiocyanato-N,S) cobalt (III) chloride  
 (D) Pentaammine (mercapto-N) cobalt (III) chloride
- Ans. (A)

## ISOMERISM IN COORDINATION COMPOUND

- (a) Compounds which have the same molecular formula, but differ in their properties due to the difference in structure are called as **Isomers**.
- (b) Isomerism is commonly considered, to be the characteristic of only organic compounds, it is also found although less frequently among inorganic substances.



(c) **Classification of isomerism :****STRUCTURAL ISOMERISM**

It arises due to the difference in the type of chemical linkages and distribution of ligands within and outside the coordination sphere.

**1. Ionisation isomers :**

The type of isomerism is due to the exchange of groups or ion between the coordinating sphere and the ionisation sphere

**Ex.**

- (a)  $\text{Co}(\text{NH}_3)_4\text{Br}_2\text{SO}_4$  can represent  
 (i)  $[\text{Co}(\text{NH}_3)_4\text{Br}_2]\text{SO}_4$  (red violet)  
 (ii)  $[\text{Co}(\text{NH}_3)_4]\text{SO}_4[\text{Br}_2]$  (red).

These complexes give sulphate ion and bromide ion respectively

- (b)  $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\text{Br}_2$  and  $[\text{Pt}(\text{NH}_3)_4\text{Br}_2]\text{Cl}_2$   
 (c)  $[\text{Co}(\text{NH}_3)_4(\text{NO}_3)_2]\text{SO}_4$  and  $[\text{Co}(\text{NH}_3)_4\text{SO}_4](\text{NO}_3)_2$

**2. Hydrate isomers :**

This type of isomerism is due to presence of different number of water molecules inside a coordination sphere.

**Ex.**  $\text{Cr}(\text{H}_2\text{O})_6\text{Cl}_3$  has three possible structure

- (i)  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$  (violet)                      (ii)  $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$  (green)  
 (iii)  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$  (dark green)

These complexes differ from one another with respect to the number of water molecules acting as ligands.

Other hydrate isomers are –

- (i)  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]\text{Cl}_2$                       (ii)  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl} \cdot \text{H}_2\text{O}$

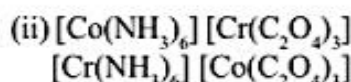
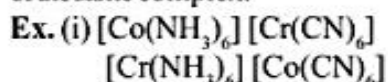
**3. Linkage or salt isomers :**

- (a) This type of isomerism arises due to presence of ambidentate ligands like  $\text{NO}_2^-$ ,  $\text{CN}^-$  and  $\text{SCN}^-$   
 (b) These ligands have two donor atoms but at a time only one atom is directly linked to the central metal atom of the complex.  
 (c) Such type of isomers are distinguished by infra red (I.R.) spectroscopy.

**Ex.** (i)  $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]\text{Cl}_2$  and  $[\text{Co}(\text{NH}_3)_5(\text{ONO})]\text{Cl}_2$   
 (ii) In  $\text{NO}_2^-$  ligand, The coordinating sites are nitrogen (i.e.,  $\text{NO}_2^-$ ) or through oxygen (i.e.  $\text{ONO}$ )  
 (iii) The nitro isomer is yellow and is stable to acids whereas nitrito isomer is red and is decomposed by acids.

**4. Coordination isomers :**

- (a) This type of isomerism is exhibited when the complex has two complex ions in it, cationic and anionic.
- (b) This type of isomerism is caused by the interchange of ligands and metal ions between the two complex ions of the same complex.

**Illustration**

1. Select correct code about complex  $[\text{Cr}(\text{NO}_2)(\text{NH}_3)_5][\text{ZnCl}_4]$   
 (I) IUPAC name of the compound is Pentaamminenitrito-N-chromium (III) tetrachloridozincate (II)  
 (II) It shows geometrical isomerism  
 (III) It shows linkage isomerism  
 (IV) It shows co-ordination isomerism  
 (A) III, IV (B) I, III & IV (C) II, III & IV (D) I, II, III & IV

**Ans. (B)**

- Sol.** (I)  $[\text{Cr}(\text{NO}_2)(\text{NH}_3)_5][\text{ZnCl}_4]$   
 IUPAC name of the compound is Pentaamminenitrito-N-chromium (III) tetrachloridozincate (II)  
 (III) It shows linkage isomerism due to presence of ambident ligands  
 $[\text{Cr}(\text{NO}_2)(\text{NH}_3)_5][\text{ZnCl}_4]$   
 $[\text{Cr}(\text{ONO})(\text{NH}_3)_5][\text{ZnCl}_4]$   
 (IV) Because both complex ions have different ligands

**Exercise**

1. Which of the following is pair of ionization isomers –  
 (A)  $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$  and  $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$   
 (B)  $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$  and  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$   
 (C)  $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$  and  $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$   
 (D) cis- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$  and trans- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$

**Ans. (A)****STEREO ISOMERISM**

- (a) They have same molecule formula, same constitution, they differ only with respect to the spatial orientation of ligands in space around the metal ion.
- (b) The two stereo isomers which are possible are - Geometrical and optical.

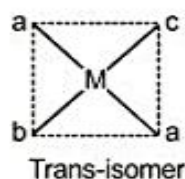
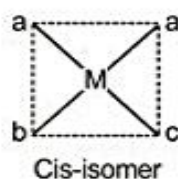
**1. Geometrical or cis - Trans isomers :**

- (a) The ligands occupy different positions around the central metal ion.
- (b) When two identical ligands are coordinated to the metal ion from the same side then it is **cis isomer**. (Latin, cis means same).
- (c) If the two identical ligands are coordinated to the metal ion from opposite side then it is **Trans isomer** (in Latin, Trans means across)
- (d) These geometrical isomers differ in physical as well as in chemical properties.
- (e) Geometrical isomerism is most important in compounds with coordination numbers 4 and 6.
- (f) 4-coordinated complexes with tetrahedral geometry do not exhibit cis-Trans isomerism.
- (g) It is exhibited by 4-coordinated complexes with square planar geometry.

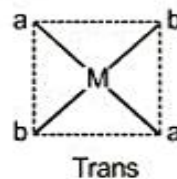
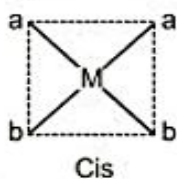


### Geometrical isomers with coordination number = 4 (Square planar complexes)

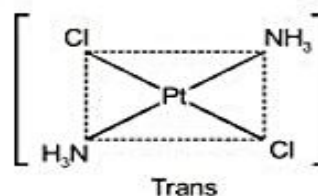
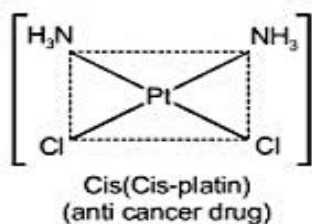
- (i) Complexes with general formula,  $\text{Ma}_2\text{b}_2$  (where both a and b are monodentate) can have Cis-and trans isomers.



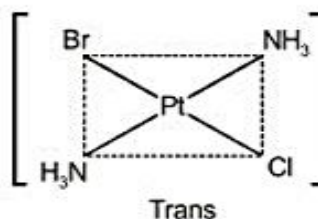
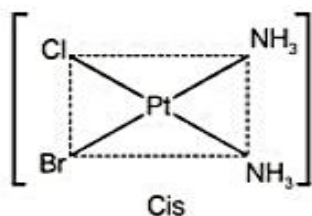
- (ii) Complexes with general formula  $\text{Ma}_2\text{b}_2\text{c}$  can have Cis-and trans-isomers.



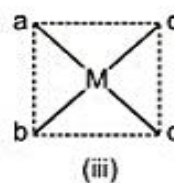
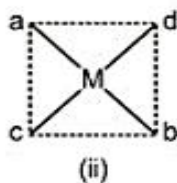
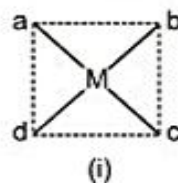
e.g.  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$



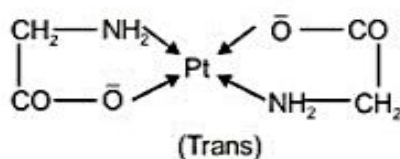
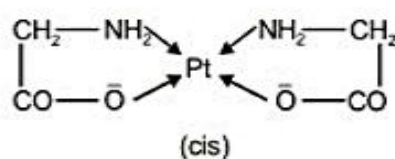
e.g.  $[\text{Pt}(\text{NH}_3)_2\text{ClBr}]$



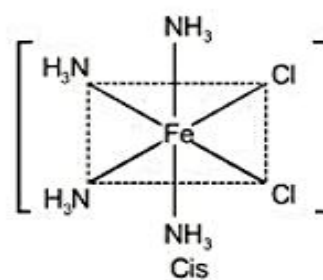
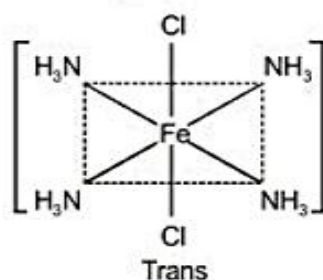
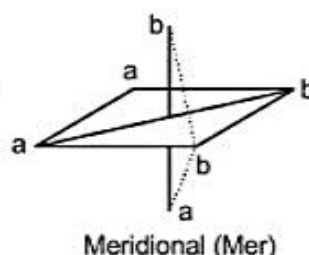
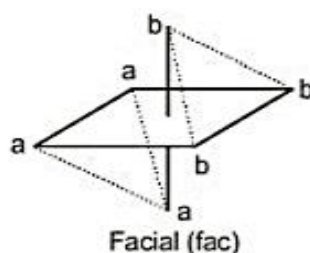
- (iii) Complexes with general formula,  $\text{Mabcd}$  can have three isomers.



- (vi) Diglycinato platinum (II) complexes



## Geometrical isomers with coordination number = 6

(i)  $[\text{Fe}(\text{NH}_3)_4\text{Cl}_2]$ (ii) Facial and Meridional isomerism ( $\text{Ma}_3\text{b}_3$ )

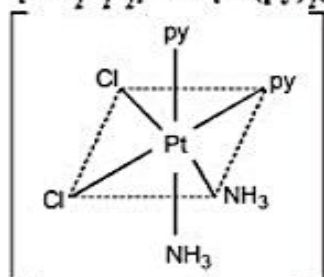
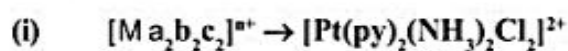
Other 6-Coordinated geometrical isomers are

General formula	Total No. of geometrical isomers
$\text{Mabcdef}$	15
$\text{Ma}_2\text{b}_2\text{c}_2$	5
$\text{Ma}_2\text{bcde}$	9
$\text{Ma}_4\text{b}_2$	2
$\text{Ma}_4\text{bc}$	2
$\text{Ma}_3\text{b}_3$	2
$\text{Ma}_6, \text{Ma}_5\text{b}$	Nil
Here M = central atom a, b, c, d, e, f = ligands (unidentate)	

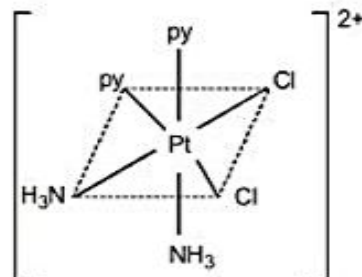
## 2. Optical isomers :

- Optically active complexes are those which are nonsuperimposable over the mirror image structure.
- An optically active complex is one which is asymmetric in nature i.e., not divisible into two identical halves.
- The complex which rotates plane polarised light to left hand side is laevo rotatory i.e., ' $\ell$ ' or ' $-$ ' and if the complex rotates the plane polarised light to right hand side then it is **dextro rotatory 'd' or '+'**.
- Thus complexes which have same physical and chemical properties but differ in their action towards plane polarised light are called as **optical isomers**.
- The ' $d$ ' and ' $\ell$ ' isomers of a compound are called as **Enantiomers or Enantiomorphs**.
- Only those 6-coordinated complexes in which there are chelating agents i.e. bidentate ligands, exhibit optical isomerism. This is due to the absence of elements of symmetry in the complex.
- Optical isomerism is not found in square planar complexes on account of the presence of axis of symmetry.

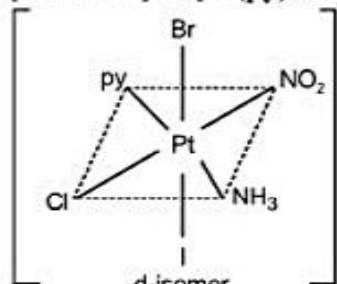
## Optical isomer with Coordination number = 6



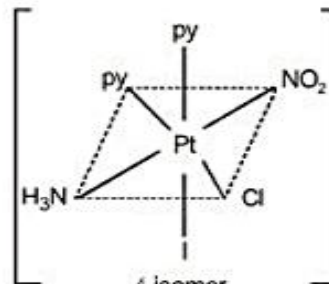
Cis-d-isomer



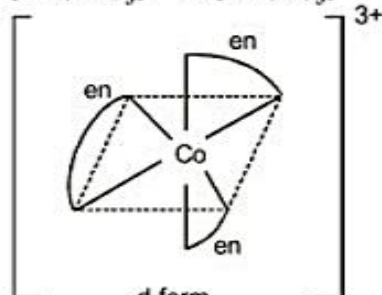
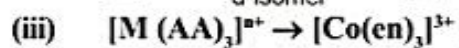
Cis-l-isomer



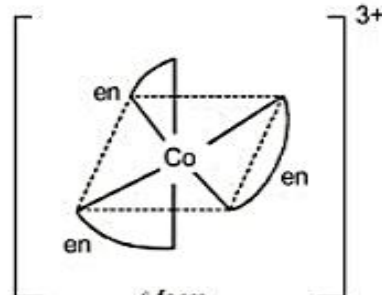
d-isomer



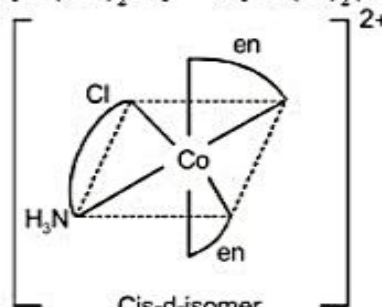
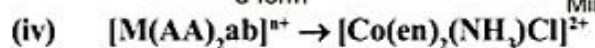
l-isomer



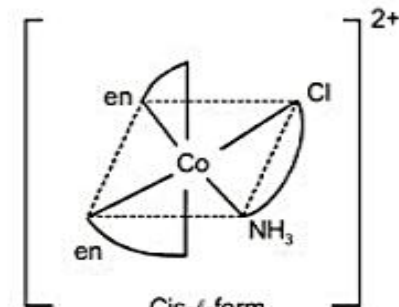
d-form



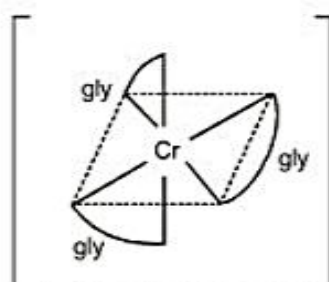
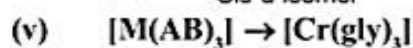
l-form



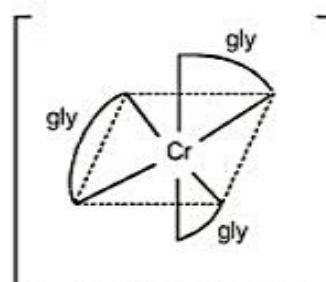
Cis-d-isomer



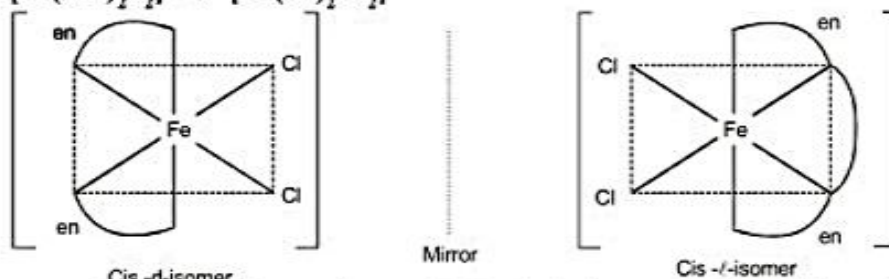
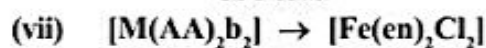
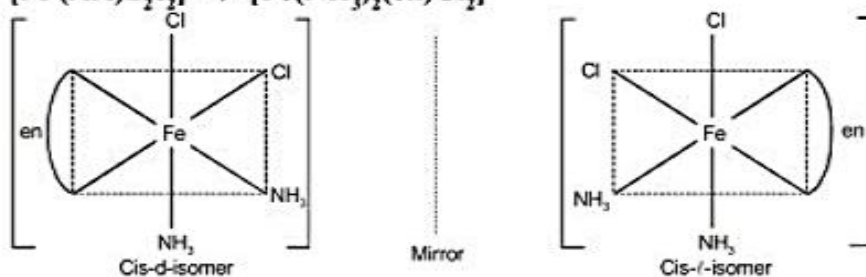
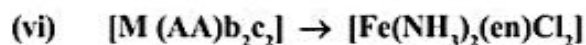
Cis-l-form



Cis or trans-d-isomer



Cis or trans-l-isomer

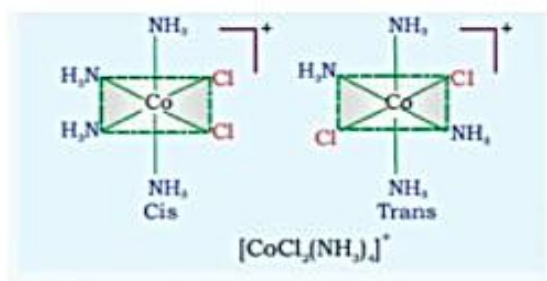


- (i) Trans-  $[Fe(en)_2Cl_2]$  do not show optical activity due to superimposition of their mirror image.  
 (ii) Some more examples are optically active:  
 $[Cr(ox)_3]^{3-}$ ;  $[Fe(dipy)_3]^{2+}$ ;  $[Cr(ox)_2(H_2O)_2]$ ;  $[Pt(en)_3]^{4+}$  etc.

### Illustration

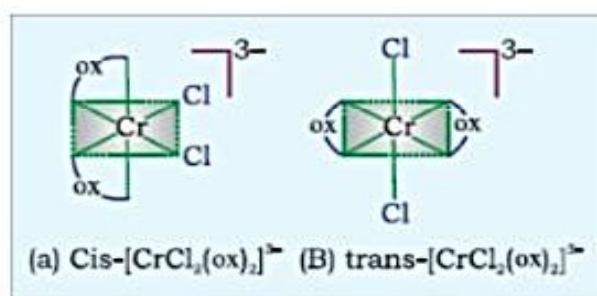
1. Draw structures of geometrical isomers of  $[CoCl_2(NH_3)_4]^+$ .

Sol.



2. Which out of the following two coordination entities is chiral (optically active)?  
 (a) cis -  $[CrCl_2(ox)_2]^{3-}$       (b) trans -  $[CrCl_2(ox)_2]^{3-}$ .

Sol. The two entities are represented as



Out of the two, (a) cis- $[CrCl_2(ox)_2]^{3-}$  is chiral (optically active).

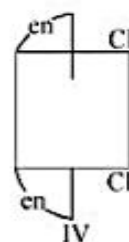
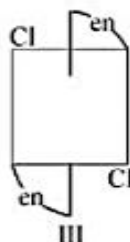
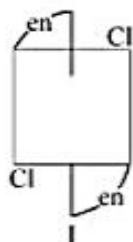


### Exercise

1.  $[\text{Co}(\text{en})_3]^{3+}$  ion is expected to show  
 (A) two optically active isomers: d and l forms  
 (B) three optically active isomers: d, l and meso forms  
 (C) four optically active isomers: cis, d and l isomers and trans d and l isomers  
 (D) none of these

Ans. (A)

2. Of the following configurations, the optical isomers are



(A) I and II

(B) I and III

(C) II and IV

(D) II and III

Ans. (C)

## BONDING IN COORDINATION COMPOUNDS

### 1. Valence Bond Theory

The salient features of the theory are summarised below.

- The central metal ion has a number of empty orbitals for accommodating electrons donated by the ligands. The number of empty orbitals is equal to the coordination number of the metal ion for the particular complex.
- The atomic orbitals (s, p or d) of the metal ion hybridize to form hybrid orbitals with definite directional properties. These hybrid orbitals now overlap with the ligand orbitals to form strong chemical bonds.
- The d-orbitals involved in the hybridization may be either inner  $(n-1)$  d orbitals or outer nd-orbitals. The complexes formed in these two ways are referred to as low spin and high spin complexes, respectively.
- Each ligand contains a lone pair of electrons.
- A covalent bond is formed by the overlap of a vacant hybridized metal orbital and a filled orbital of the ligand. The bond is also sometimes called as a coordinate bond.
- If the complex contains unpaired electrons, it is paramagnetic in nature, while if it does not contain unpaired electrons, it is diamagnetic in nature.
- The number of unpaired electrons in the complex, points out the geometry of the complex as well as hybridisation of central metal ion and vice-versa. In practice, the number of unpaired electrons in a complex is found from magnetic moment measurements as illustrated below.

$$\mu_s = \sqrt{n(n+2)}, \text{ where } n = \text{no of unpaired electron}$$

Thus the knowledge of the magnetic moment can be of great help in ascertaining the type of complex

- Under the influence of a strong ligand, the electrons can be forced to pair up against the Hund's rule of maximum multiplicity.

### Draw back of valence bond Theory

- (i) It describes bonding in coordination compounds only qualitatively
- (ii) It does not offer any explanation for the optical absorption spectra of complex
- (iii) It does not describe the detailed magnetic properties of coordination compounds.

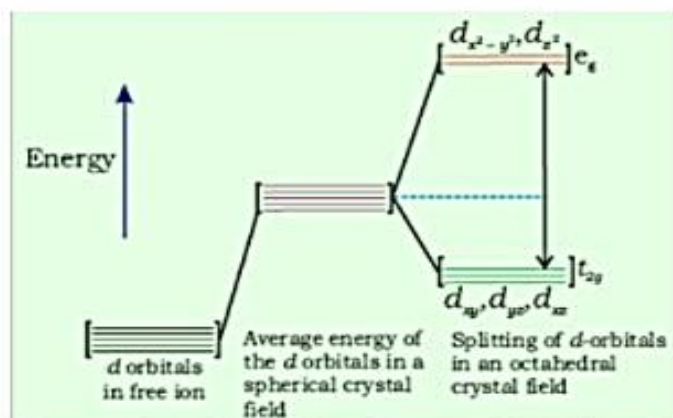
### Crystal field Theory

This is the more advanced theory and satisfactorily explains the optical absorption spectra and magnetic properties of complexes which were not explained by V.B.T. But its details are beyond the scope of this text.

**The shape of complexes depends upon hybridization state of central atom, it is described as follows:**

### Octahedral complexes

On the basis of hybridized orbitals it can be of two type as  $d^2sp^3$  (inner orbital) or  $sp^3d^2$  (outer orbital) hybridized. Let us assume that the six ligands are positioned symmetrically along the cartesian axes, with the metal atom at the origin. As the ligands approach, first there is an increase in the energy of d orbitals relative to that of the free ion just as would be the case in a spherical field. Next, the orbitals lying along the axes ( $d_{z^2}$  and  $d_{x^2-y^2}$ ) get repelled more strongly than  $d_{xy}$ ,  $d_{yz}$  and  $d_{zx}$  orbitals, which have lobes directed between the axes. The  $d_{z^2}$  and  $d_{x^2-y^2}$  orbitals get raised in energy and  $d_{xy}$ ,  $d_{yz}$ ,  $d_{zx}$  orbitals are lowered in energy relative to the average energy in the spherical crystal field. Thus, the degenerate set of d orbitals get split into two sets: the lower energy orbital set,  $t_{2g}$  and the higher energy,  $e_g$  set. The energy separation is denoted by  $\Delta_o$  (the subscript o is for octahedral) :



**Figure : d-orbital splitting in an octahedral crystal field**

### Inner orbital complexes :

We have already discussed that in these type of complexes the d-orbitals used are of lower quantum number i.e.  $(n - 1)$  various examples are as follow

- (a) Complexes formed by the use of inner orbitals are diamagnetic or have reduced paramagnetism.
- (b) These are called as low spin or spin paired complexes

### $[\text{Fe}(\text{CN})_6]^{4-}$

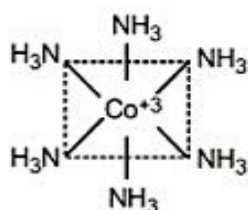
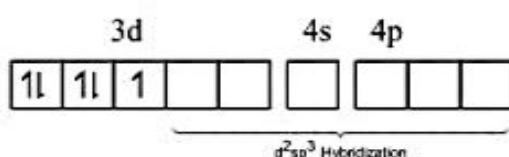
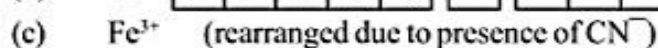
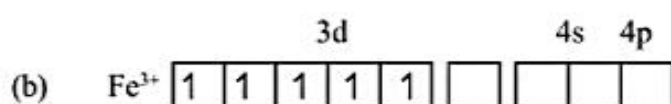
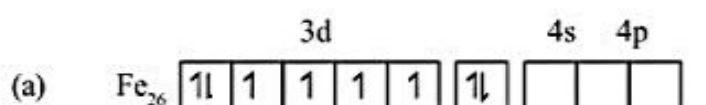
- (a) electronic configuration of  $\text{Fe}^{26} = [\text{Ar}] 3d^6 4s^2$

- (b) electronic configuration of  $\text{Fe}^{+2} = [\text{Ar}] 3d^6$  = 

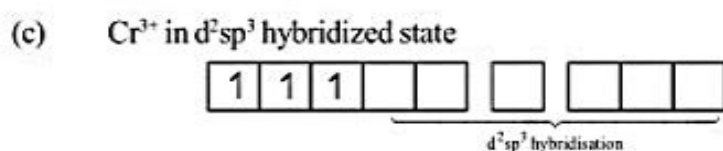
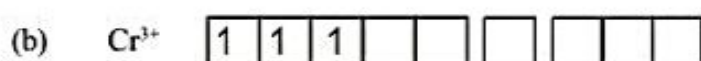
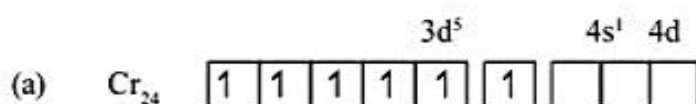
1↓	1	1	1	1			
----	---	---	---	---	--	--	--
- (c) electronic configuration of  $\text{Fe}^{+2}$  after rearrangement = 

1↓	1↓	1↓					
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 $d^2sp^3$
- (d) The above rearrangement is due to presence of cyanide ligand
- (e) In this state  $\text{Fe}^{2+}$  undergoes  $d^2sp^3$  hybridisation to form six  $d^2sp^3$  hybrid orbitals, each of which accepts electron pair donated by  $\text{CN}^-$  ions.
- (f) The resultant complex is inner octahedral as shown in figure and it should be diamagnetic as it has no unpaired electron. Formation of  $[\text{Co}(\text{NH}_3)_6]^{3+}$  takes place in the same manner

Octahedral shape of  $[\text{Co}(\text{NH}_3)_6]^{3+}$  **$[\text{Fe}(\text{CN})_6]^{3-}$** 

- (d) The resulting complex is octahedral due to  $d^2sp^3$  hybridization
- (e) Due to presence of unpaired electron it is paramagnetic

 **$[\text{Cr}(\text{NH}_3)_6]^{3+}$** 



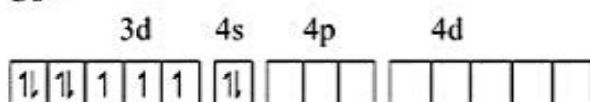
- (d) This  $d^2sp^3$  hybridisation leads to octahedral geometry, the complex  $[\text{Cr}(\text{NH}_3)_6]^{3+}$  will be octahedral in shape
- (e) Since the complex ion has 3 unpaired electrons so it must be paramagnetic.
- (f) Other complexes of chromium with similar inner structure are  $[\text{Cr}(\text{CN})_6]^{3-}$  and  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$

### Outer orbital complexes

- (a) In these complexes s, p as well as d orbitals involved in hybridization, belong to the highest quantum number (n)
- (b) Complexes formed by the use of outer n, d orbitals will be paramagnetic.
- (c) These complexes are called high-spin or spin free complexes
- (d) The outer orbital complexes have greater number of unpaired electrons.

### $[\text{CoF}_6]^{3-}$

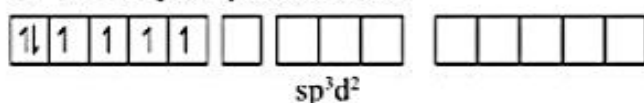
- (a)  $\text{Co}^{27}$



- (b)  $\text{Co}^{3+}$  ion



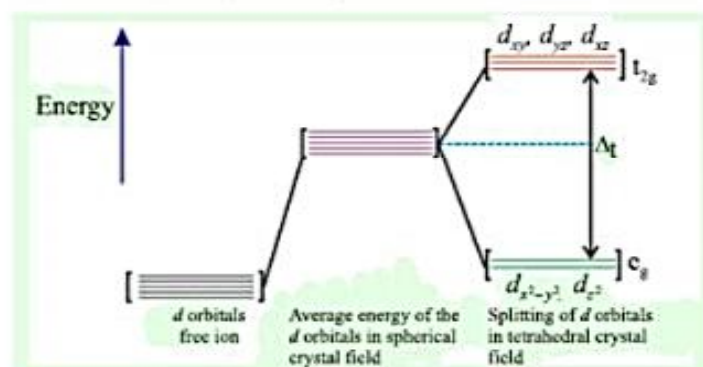
- (c)  $\text{Co}^{3+}$  ion in  $sp^3d^2$  hybridised state



- (d) Due to octahedral orientation of six  $sp^3d^2$  hybridised orbitals shape  $[\text{CoF}_6]^{3-}$  complex ion is octahedral
- (e) Due to presence of four unpaired electrons in 3d orbital  $[\text{CoF}_6]^{3-}$  ion has paramagnetic character
- (f) Other examples are  $[\text{FeF}_6]^{3-}$ ,  $[\text{Fe}(\text{NH}_3)_6]^{2+}$ ,  $[\text{Ni}(\text{NH}_3)_6]^{2+}$ ,  $[\text{Cu}(\text{NH}_3)_6]^{2+}$ ,  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$

### Tetrahedral Complexes :

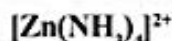
In tetrahedral coordination entity formation, the 'd' orbital splitting is inverted and smaller as compared to the octahedral field splitting. For the same metal, the same ligands and metal-ligand distances, it can be shown that  $\Delta_t = -(4/9)\Delta_o$ . Consequently, the orbital splitting energies are not sufficiently large for forcing pairing and, therefore, low spin configurations are rarely observed.



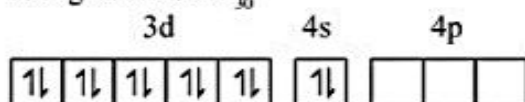
**Figure : d-orbital splitting in an tetrahedral crystal field**



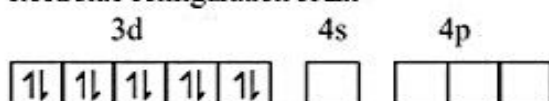
These are formed by  $sp^3$  hybridisation. Complexes of  $Zn^{2+}$  are invariable tetrahedral because they involve  $sp^3$  hybrid orbitals



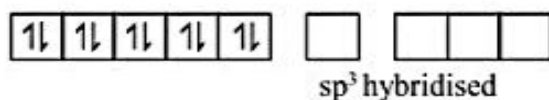
- (a) configuration of  $Zn_{30}$



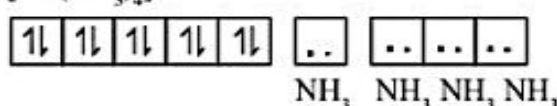
- (b) electronic configuration of  $Zn^{2+}$



- (c)  $Zn^{2+}$  in  $sp^3$  hybridised state



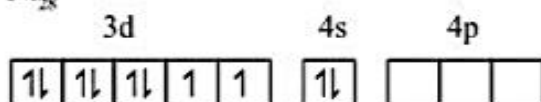
- (d)  $[Zn(NH_3)_4]^{2+}$



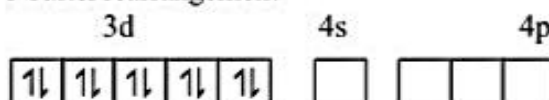
- (e) Since the complex is formed by  $sp^3$  hybridisation, it is tetrahedral  
 (f) Since all electrons are paired it is diamagnetic



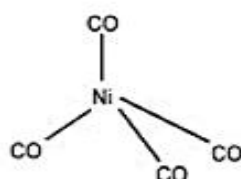
- (a)  $Ni_{28}$



- (b) Ni after rearrangement



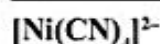
- (c) The empty one 4s and three 4p orbitals mix to form four  $sp^3$  hybridised orbitals  
 (d) each orbital accepts one electron pair from carbon monoxide molecule forming  $[Ni(CO)_4]$   
 (e) The shape of nickel tetra carbonyl is tetrahedral as shown below  
 (f) It is diamagnetic in nature



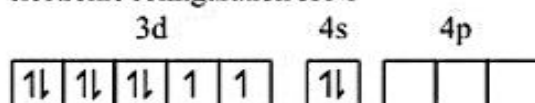
#### Square planar complex.

These are formed due to  $dsp^2$  hybridisation.

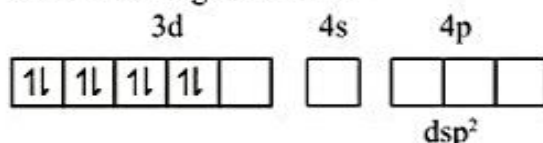
These complexes tend to be formed when the central ion has only one d orbital available in the inner shell



(a) electronic configuration of Ni



(b) electronic configuration of  $\text{Ni}^{2+}$

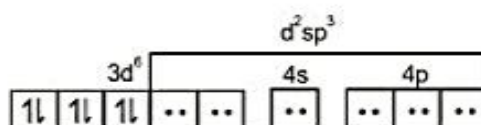
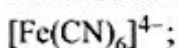


- (c) The rearrangement is due to presence of strong ligand  $\text{CN}^-$ . The four orbitals make  $dsp^2$  hybridisation  
 (d) The shape of resulting complex is square planar  
 (e) Due to paired electrons it is diamagnetic.

### Illustration

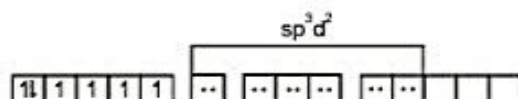
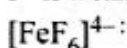
1.  $[\text{Fe}(\text{CN})_6]^{4-}$  is diamagnetic while  $[\text{FeF}_6]^{4-}$  is strongly paramagnetic. Why?

**Sol.**  $\text{CN}^-$  is strong field ligand and so it pairs up the electrons leading to the formation of low spin complex which is diamagnetic.



Octahedral, diamagnetic complex

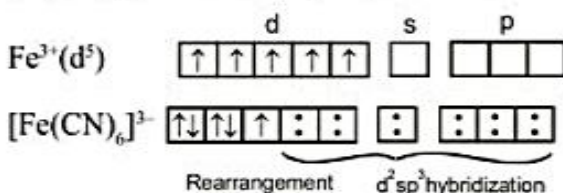
$\text{F}^-$  is weak field ligand so it forms high spin paramagnetic complex.



Octahedral, paramagnetic complex

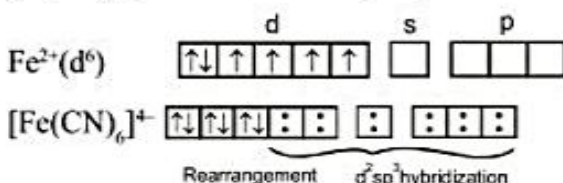
2.  $[\text{Fe}(\text{CN})_6]^{3-}$  is weakly paramagnetic while  $[\text{Fe}(\text{CN})_6]^{4-}$  is diamagnetic, why?

**Sol.**  $[\text{Fe}(\text{CN})_6]^{3-}$  involves  $d^2sp^3$  hybridization



One d-orbital is singly occupied, hence it is weakly paramagnetic in nature.

$[\text{Fe}(\text{CN})_6]^{4-}$  involves also  $d^2sp^3$  hybridization but it has  $\text{Fe}^{2+}$  ion as central ion.



All orbitals are doubly occupied, hence it is diamagnetic in nature.

### Exercise

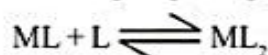
- Hexafluorocobaltate(III) ion is found to be high spin complex, the hybridisation state of cobalt is –  
 (A)  $d^2sp^3$  (B)  $sp^3$  (C)  $sp^3d$  (D)  $sp^3d^2$   
**Ans. (D)**
- The number of unpaired electrons calculated in  $[Co(NH_3)_6]^{3+}$  and  $[CoF_6]^{3-}$  are :  
 (A) 4 and 4 (B) 0 and 2 (C) 2 and 4 (D) 0 and 4  
**Ans. (D)**
- For the  $t_{2g}^6 e_g^2$  system, the value of magnetic moment ( $\mu$ ) is –  
 (A) 2.83 B.M. (B) 1.73 B.M. (C) 3.87 B.M. (D) 4.92 B.M.  
**Ans. (A)**
- Which of the following electronic arrangement gives the highest value of the magnetic moment in case of octahedral complex ?  
 (A)  $d^6$ , strong field (B)  $d^7$ , high spin (C)  $d^4$ , weak field (D)  $d^2$ , strong field  
**Ans. (C)**

### STABILITY OF COMPLEX

- A complex is formed in solution by the stepwise addition of ligands to a metal ion
- This can be expressed as follows  $M + L \rightleftharpoons ML$ , where M = metal and L is ligand
- The stability constant K for this reaction is as shown

$$K = \frac{ML}{[M][L]}$$

- This metal can again get a ligand



- The forthcoming stability constant  $K_1$  then  $K_1 = \frac{[ML_2]}{[ML][L]}$  its value is less than K
- The higher the value of stability constant stabler is the complex.
- The value of stability constants for some of the complexes are given below :

Complex	Stability constant
$[Cu(NH_3)_4]^{2+}$	$4.5 \times 10^{11}$
$[Ag(NH_3)_2]^+$	$1.6 \times 10^7$
$[Co(NH_3)_6]^{2+}$	$1.12 \times 10^6$
$[Co(NH_3)_6]^{3+}$	$5.0 \times 10^{33}$
$[AgCl_2]^-$	$1.11 \times 10^5$
$[AgBr_2]^-$	$1.28 \times 10^7$
$[Ag(CN)_2]^-$	$1.0 \times 10^{22}$
$[Cu(CN)_4]^{2-}$	$2.0 \times 10^{27}$
$[Fe(CN)_6]^{3-}$	$7.69 \times 10^{43}$



## Factors influencing the stability of complex

### Nature of central ion -

- The complex will be more stable for higher values of charge density  $\left(\frac{\text{Charge}}{\text{radius}}\right)$
- The higher the electronegativity of the central ion, the greater is the stability of its complexes
- The higher the oxidation state of the metal the more stable is the compound

### Nature of ligand

- A basic ligand is likely to easily donate its electrons. Thus a more basic ligand will form more stable complex.
- Chelating ligands form more stable complexes as compared to monodentate ligands.

## ORGANOMETALLIC COMPOUNDS

Compounds containing at least one metal-carbon bond may be called organometallic compounds. These compounds may be defined as those compounds in which the carbon atoms of organic groups are linked to metal atoms. The compounds of elements such as boron, phosphorus, silicon, germanium, tellurium and antimony with organic groups are also included in the organometallics.

### 1. $\sigma$ -bonded organometallic compounds :

In  $\sigma$ -bonded compound organic group is bonded to metal atoms through a normal 2 electron covalent bond. Some example of  $\sigma$ -bonded organometallic compounds are as below –

$\text{Al}_2(\text{CH}_3)_6$ ,  $\text{Al}_2(\text{C}_6\text{H}_5)_6$ ,  $\text{Pb}(\text{CH}_3)_4$ ,  $\text{Pb}(\text{C}_2\text{H}_5)_4$ ,  $\text{Zn}(\text{C}_2\text{H}_5)_4$ ,  $(\text{CH}_3)_4\text{Sn}$  etc.

#### Examples :

$\text{R} - \text{Mg} - \text{X}$	$(\text{CH}_3\text{CH}_2)_2\text{Zn}$
Grignard reagent (Alkyl magnesium halide)	Diethyl zinc
$(\text{CH}_3)_4\text{Si}$	$(\text{CH}_3)_4\text{Sn}$
Tetramethyl silane	Tetramethyl tin
$(\text{C}_2\text{H}_5)_4\text{Pb}$	$(\text{CH}_3)_2\text{Cd}$
Tetraethyl lead	Dimethyl cadmium

Trimethyl aluminium exists as stable dimer. In this, two methyl groups act as bridges between two aluminium atoms. The alkyl bridge is formed by multicentre bonding.

### 2. $\pi$ -bonded organometallic compounds :

This type of compounds are generally formed by transition metals. Some examples of  $\pi$ -complexes are: Ferrocene, Dibenzene chromium, Zeise's salt, etc. are some well known examples of the complexes belonging to this class.

### 3. $\sigma$ - and $\pi$ -bonded organometallic compounds :

Metal carbonyls of transition metals constitute another important class of organometallic compounds. The first metal carbonyls,  $\text{Ni}(\text{CO})_4$  and  $\text{Fe}(\text{CO})_5$ , were discovered by A. Mond in 1890 and 1891. Few more examples of metal carbonyls are  $\text{Cr}(\text{CO})_6$ ,  $\text{Mo}(\text{CO})_6$ . In addition to mononuclear of metal carbonyls mentioned above, transition metals form various polynuclear metals carbonyls such as  $\text{Fe}(\text{CO})_{12}$ ,  $\text{Mn}_2(\text{CO})_{10}$ . The metal carbonyl bond in metal carbonyls posses both  $\sigma$  and  $\pi$  character.



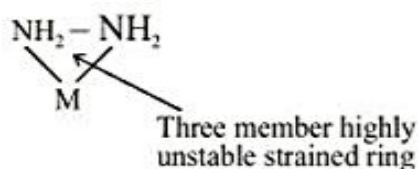
### Application of Organometallic Compounds :

- (a) **Ziese's salt** is used in the treatment of cancer.
- (b) Nickel tetracarbonyl is used in purification of nickel.
- (c) Ethylmercuricchloride is used as a fungicide.
- (d) As homogeneous Catalyst  
**Wilkinsons catalyst** for hydrogenation of olefins is  $[P(Ph)_3RhCl]$
- (e) As heterogeneous catalyst  
**Zeigler-Natta Catalyst** ( $R_3Al + TiCl_4$ )  
 (Tri alkyl Aluminium + Titanium tetrachloride) used for polymerisation of alkene.
- (f) **Organic synthesis:** OMC like  $RMgX$ ,  $R_2Cd$ ,  $CH_3Li$  etc. are used for preparation of almost all type of organic compounds.
- (g) **Cyclopentadienyl manganesetricarbonyl** and **TEL** (Tetraethyl lead) is used as antiknock agent in petrol.
- (h) In medicine – Organo arsenic compounds are used as medicine for syphilis disease.
- (i) In agriculture– Seeds are treated with ethyl mercury Chloride commercially known as **CERESSAN** to protect the plants against infection.

## SOLVED EXAMPLES

**Q.1**  $\text{NH}_2.\text{NH}_2$  although possesses two electron pair for donation but not acts as chelating agent. Why?

**Sol.** The co-ordinating by  $\text{NH}_2.\text{NH}_2$  leads to a three member highly unstable strained ring and thus it does not acts as chelating agent.



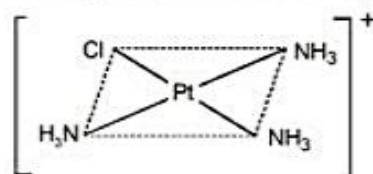
**Q.2** Square planar complexes with co-ordination number four exhibit geometrical isomerism whereas tetrahedral complexes do not. Why?

**Sol.** In tetrahedral complexes, the relative position of atoms with respect to each other is same thus these do not show geometrical isomerism. Square planar complexes show cis, trans isomerism.

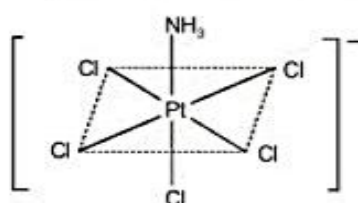
**Q.3** Platinum (II) forms square planar complexes and plantinum (IV) gives octahedral complexes. How many geometrical isomers are possible for each of the following complexes? Describe their structures -

(a)  $[\text{Pt}(\text{NH}_3)_3\text{Cl}]^+$  (b)  $[\text{Pt}(\text{NH}_3)\text{Cl}_5]^-$  (c)  $[\text{Pt}(\text{NH}_3)_2\text{ClNO}_2]$  (d)  $[\text{Pt}(\text{NH}_3)_4\text{ClBr}]^{2+}$

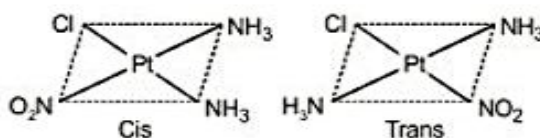
**Sol.** (a) Square planar complex of the type  $\text{Ma}_3\text{b}$  shows no isomerism.



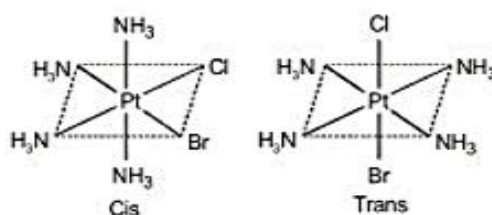
(b) An octahedral complex of the type  $\text{Ma}_5\text{b}$  shows no isomerism.



(c) A square planar complex of the type  $\text{Ma}_2\text{bc}$  exists as cis and trans isomers

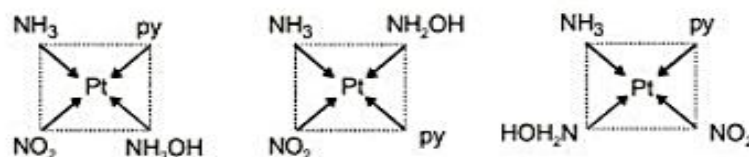


(d) An octahedral complex of the type  $\text{Ma}_4\text{bc}$  shows cis and trans isomerism.



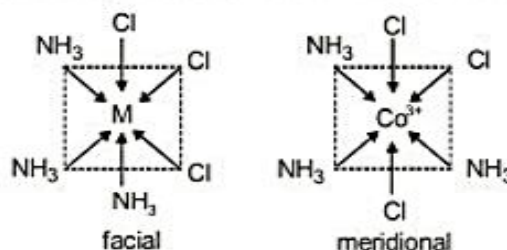
**Q.4** How many geometrical isomers with formula  $[MABCD]$  e.g.,  $[\text{Pt}(\text{NH}_3)\text{py}(\text{NH}_2\text{OH})\text{NO}_2]^+$  are possible?

**Sol.** Three isomers



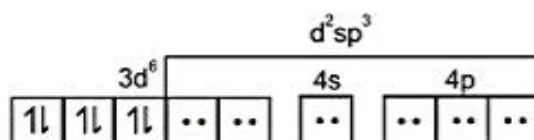
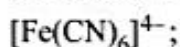
**Q.5** What are facial and meridional isomers? Explain with examples.

**Sol.** For the complexes of the type  $[\text{Ma}_3\text{b}_3]$  e.g.,  $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$  and  $[\text{Rh}(\text{py})_3\text{Cl}_3]$ ; the isomer is called facial (fac) when all similar ligands occupy same face of an octahedron as shown below. When all similar ligands are not on the same face then isomer is called meridional (mer).



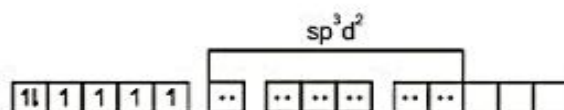
**Q.6**  $[\text{Fe}(\text{CN})_6]^{4-}$  is diamagnetic while  $[\text{FeF}_6]^{4-}$  is strongly paramagnetic. Why?

**Sol.**  $\text{CN}^-$  is strong field ligand and so it pairs up the electrons leading to the formation of low spin complex which is diamagnetic.



Octahedral, diamagnetic complex

$\text{F}^-$  is weak field ligand so it forms high spin paramagnetic complex.



Octahedral, paramagnetic complex

**Q.7** If excess of  $\text{AgNO}_3$  solution is added to 100 mL of a 0.024 M solution of dichlorobis (ethylene diamine) cobalt (III) chloride, how many mol of  $\text{AgCl}$  be precipitated:

- (A) 0.0012 (B) 0.0016 (C) 0.0024 (D) 0.0048

**Ans.** (C)

**Sol.**  $[\text{CoCl}_2(\text{en})_2]\text{Cl} \xrightarrow{\text{AgNO}_3} [\text{CoCl}_2(\text{en})_2]\text{NO}_3 + \text{AgCl}$

Mole of  $[\text{CoCl}_2(\text{en})_2]\text{Cl}$  = molarity  $\times$  v(Lt.)

0.0024 mole of  $[\text{CoCl}_2(\text{en})_2]\text{Cl}$  gives

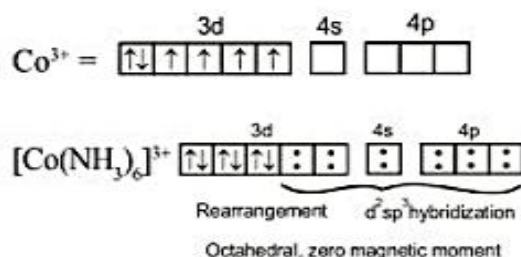
$$\frac{100}{1000} \times 0.024 = 0.0024 \text{ mole of } \text{Cl}^-$$

Which precipitate 0.0024 mole of  $\text{AgNO}_3$  because 1 mole  $\text{Ag}^+$  required 1 mole  $\text{Cl}^-$  to precipitate

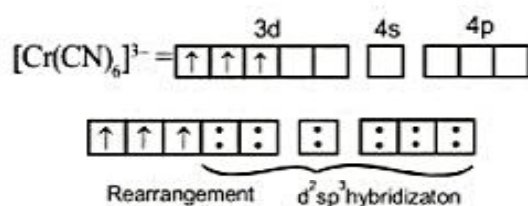
**Q.8** Find out the hybridization, geometry and magnetic moment of the complexes :



**Sol.** (i) The oxidation state of cobalt in the complex is +3. The electronic configuration of  $\text{Co}^{3+}$  ions is



(ii) The oxidation state of chromium in the complex is +3. The electronic configuration of  $\text{Cr}^{3+}$  ion is



Octahedral, magnetic moment

$$= \sqrt{3 \times (3+2)} = \sqrt{15} = 3.87 \text{ B.M.}$$

**Q.9** The magnetic moment of  $[\text{MnCl}_4]^{2-}$  is 5.92 B.M. On the basis of its magnetic moment, write configuration of  $\text{Mn}^{2+}$  in this complex.

**Sol.** For an atom/ion

$$\text{Magnetic moment } (\mu) = \sqrt{n(n+2)}$$

(n = No. of unpaired electrons)

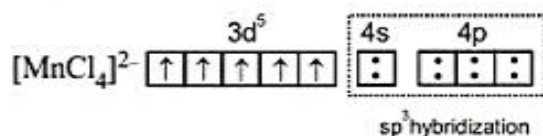
Given that  $\mu = 5.92 \text{ B.M.}$

$$\therefore 5.92 = \sqrt{n(n+2)}$$

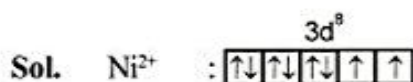
or  $n = 5$

Thus in this complex Mn contains five unpaired electrons and so its possible configuration may be  $\text{Mn}^{2+}$  in  $[\text{MnCl}_4]^{2-} = [\text{Ar}] 3d^5 4s^0$

so hybridisation of  $\text{Mn}^{2+}$  in the given complex must be  $sp^3$ .



**Q.10** All the octahedral complexes of  $\text{Ni}^{2+}$  are outer orbital complexes, why?

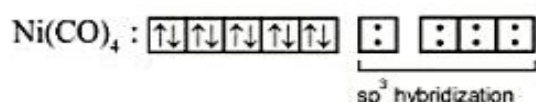
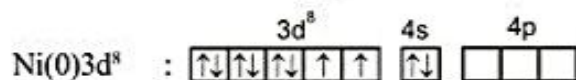


Thus only one vacant 3d-orbital is available after pairing up of electrons due to strong field ligand. Therefore,  $d^2sp^3$  hybridisation is not possible. Only  $sp^3d^2$  is possible which represents an outer complex.

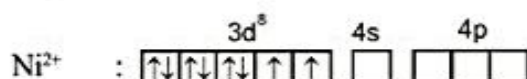


**Q.11**  $\text{Ni}(\text{CO})_4$  possesses tetrahedral geometry while  $[\text{Ni}(\text{CN})_4]^{2-}$  is square planar, why?

**Sol.** In the formation of  $\text{Ni}(\text{CO})_4$ , nickel undergoes  $sp^3$  hybridization, hence it is tetrahedral in shape.



In the formation of  $[\text{Ni}(\text{CN})_4]^{2-}$ ,  $\text{Ni}^{2+}$  ion undergoes  $dsp^2$  hybridisation, hence it is square planar in shape.



**Q.12** Consider the following complexes –

(i)  $\text{K}_2\text{PtCl}_6$                       (ii)  $\text{PtCl}_4 \cdot 2\text{NH}_3$                       (iii)  $\text{PtCl}_4 \cdot 3\text{NH}_3$                       (iv)  $\text{PtCl}_4 \cdot 5\text{NH}_3$

Their electrical conductances in aq. solutions are –

(A) 256, 0, 97, 404                      (B) 404, 0, 97, 256                      (C) 256, 97, 0, 404                      (D) 404, 97, 256, 0

**Sol.** (A) Coordination number of Pt is 6 hence

I  $\text{K}_2[\text{PtCl}_6]$  – Three ions

II  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_4]$  – Zero ions

III  $[\text{Pt}(\text{NH}_3)_3\text{Cl}_3]\text{Cl}$  – Two ions

IV  $[\text{Pt}(\text{NH}_3)_5\text{Cl}]\text{Cl}_3$  – Four ions

**Conductivity  $\propto$  no. of ions**

**Q.13** Determine the oxidation state of metal in the complex ion,  $[\text{PtCl}_6]^{2-}$ .

**Sol.** Charge on the complex ion = Oxidation state of metal + charge on ligands

$$-2 = x + 6 \times (-1)$$

$$\text{or } x = +4$$

The oxidation of Pt in the complex ion is +4.

**Q.14** The pair in which both species have same magnetic moment (spin only value) is –

(A)  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ ,  $[\text{CoCl}_4]^{2-}$                       (B)  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ ,  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$

(C)  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ ,  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$                       (D)  $[\text{CoCl}_4]^{2-}$ ,  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$

**Ans.** (B)

**Sol.** Same magnetic moment = same number of unpaired electrons =  $\sqrt{n(n+2)}$

where  $n$  = number of unpaired electrons

$\text{Co}^{2+} = 3d^7$ , 3 unpaired electrons

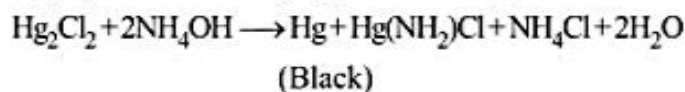
$\text{Cr}^{2+} = 3d^4$ , 4 unpaired electrons

$\text{Mn}^{2+} = 3d^5$ , 5 unpaired electrons

$\text{Fe}^{2+} = 3d^6$ , 4 unpaired electrons

**Q.15** The colour of  $\text{Hg}_2\text{Cl}_2$  changes from white to black when treated with  $\text{NH}_3$ . Why?

**Sol.**  $\text{Hg}_2\text{Cl}_2$  reacts with  $\text{NH}_3$  to give black complex.



**Q.16** Write the formula of the following complexes.

(i) Pentamminechlorocobalt (III) ion

(ii) Lithium tetrahydridoaluminate (III)

**Sol.** (i)  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ ; (ii)  $\text{Li}[\text{AlH}_4]$

**Q.17** Identify the complexes which are expected to be coloured and explain.

(A)  $\text{Ti}(\text{NO}_3)_4$

(B)  $[\text{Cu}(\text{NCCH}_3)_4]^+ \text{BF}_4^-$

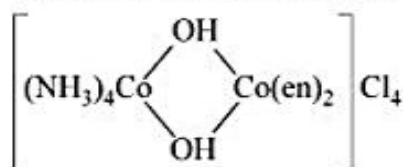
(C)  $[\text{Cr}(\text{NH}_3)_6]^{3+} 3\text{Cl}^-$

(D)  $\text{K}_3[\text{VF}_6]$

**Ans.** (C) and (D)

**Sol.** Are coloured because  $\text{Cr}^{3+}$  in  $[\text{Cr}(\text{NH}_3)_6]^{3+}$  and  $\text{V}^{3+}$  in  $[\text{VF}_6]^{3-}$  have  $3d^3$  and  $3d^2$  configuration respectively and thus show d-d transition.

**Q.18** Write the IUPAC name of the given compound.

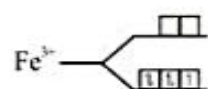


**Sol.** Tetraamine cobalt (III) di- $\mu$ -hydroxo bis ethylenediamine cobalt (III) chloride.

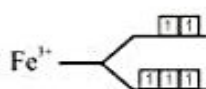
**Q.19** Explain the following with appropriate reasons :

$[\text{Fe}(\text{CN})_6]^{3-}$  ion has magnetic moment 1.73 BM, while  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  has a magnetic moment 5.92 BM.

**Sol.**  $1.73 = \sqrt{n(n+2)}$   $5.92 = \sqrt{n(n+2)}$   
 $n = 1$   $n = 5$



Due to strong field ligands ( $\text{CN}^-$ )



Due to weak ligands ( $\text{H}_2\text{O}$ )

# RADIOACTIVITY

## 1. RADIOACTIVITY

"Radioactivity is a process in which nuclei of certain elements undergo spontaneous disintegration without excitation by any external means."

**Henry Becquerel (1891)** observed the spontaneous emission of invisible, penetrating rays from potassium uranyl sulphate  $K_2UO_2(SO_4)_2$ , which influenced photographic plate in dark and were able to produce luminosity in substances like ZnS.

Later on, **Madam Marie Curie and her husband P. Curie** named this phenomenon of spontaneous emission of penetrating rays as, **Radioactivity**. They also pointed out that radioactivity is a characteristic property of an unstable or excited nucleus, i.e., a nuclear property is **independent** of all the external conditions such as pressure, temperature, nature of other atoms associated with unstable atom but **depends** upon the amount of unstable atom.

**Curies** also discovered a new radioactive element Radium from pitchblende (an ore of U i.e.  $U_3O_8$ ) which is about 3 million times more radioactive than uranium. Now a days about 42 radioactive elements are known.

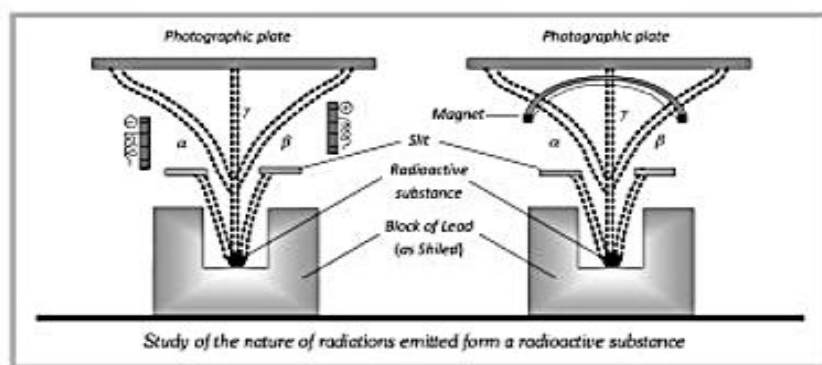
The elements whose atoms disintegrate and emit radiations are called radioactive elements.

Radioactivity can be detected and measured by a number of devices like ionisation chamber, **Geiger Muller** counter, proportional counter, flow counter, end window counter, scintillation counter, Wilson cloud chamber, electroscope, etc. The proper device depends upon the nature of the radioactive substance and the type of radiation emitted. Geiger Muller counter and proportional counter are suitable for solids and liquids, ionisation chamber is most suitable for gases.

Lightest radioactive isotope is tritium ( ${}_1H^3$ ); other lighter radioactive nuclides are  ${}^{14}C$ ,  ${}^{40}K$  and  ${}^{99}Tc$ .

## 2. NATURE OF RADIOACTIVE EMISSIONS

The nature of the radiations emitted from a radioactive substance was investigated by **Rutherford (1904)** by applying electric and magnetic fields to the radiation as shown in figure.



It is observed that on applying the field, the rays emitted from the radioactive substances are separated into three types, called  $\alpha$ ,  $\beta$ , and  $\gamma$ -rays. The  $\alpha$ -rays are deflected in a direction which shows that they carry positive charge; the  $\beta$ -rays are deflected in the opposite direction showing that they carry negative charge and the  $\gamma$ -rays are not deflected at all showing that they carry no charge.



### 3. CHARACTERISTICS OF RADIOACTIVE RAYS

Radioactive rays are characterised by the following properties:

- (i) They blacken photographic plates.
- (ii) They pass through thin metal foils.
- (iii) They produce ionization in gases through which they passes.
- (iv) They produce luminescence in zinc sulphide, barium platinocyanide, calcium tungstate, etc.

Radioactive radiations are composed of three important rays, namely  $\alpha$ ,  $\beta$  and  $\gamma$ -rays which differ very much in their nature and properties, e.g. penetrating power, ionising power and effect on photographic plates. Remember that  $\gamma$ -rays are not produced simultaneously with  $\alpha$  and  $\beta$ -rays but are produced subsequently.

#### 3.1 Properties of $\alpha$ , $\beta$ -particles and $\gamma$ -rays.

S.No	Property	$\alpha$ -Particles	$\beta$ -Particles	$\gamma$ -rays
1.	Nature and value of charge	Positive and double of the charge of the proton	Negative and equal to the charge of electron $1.6 \times 10^{-19} \text{ C}$	Uncharged (Neutral)
2.	Nature of particle	Doubly ionized helium atom (2 protons and 2 neutrons)	Electron (or) positron	Electromagnetic waves
3.	Mass	Four times the mass of the proton ( $4 \times 1.67 \times 10^{-27} \text{ kg}$ )	Equal to the mass of electron $9.1 \times 10^{-31} \text{ kg}$	Mass less
4.	Specific charge $\frac{q}{m}$	$\frac{3.2 \times 10^{-19}}{4 \times 1.67 \times 10^{-27}} = 4.79 \times 10^7$	$1.7 \times 10^{11} \text{ C kg}^{-1}$	Uncharged and mass less
5.	Explained by	Tunnel effect	Neutrino hypothesis	Transitions of nuclei into the ground energy level after $\alpha$ and $\beta$ decay
6.	Effect of electric and magnetic fields	Deflected by electric and magnetic fields	Deflected by electric and magnetic fields	Unaffected
7.	Penetrating power	1	100	10000
8.	Ionizing power	100000	100	1
9.	Velocity	Less than the velocity of light ( $1.4 \times 10^7 \text{ m/s}$ to $2.2 \times 10^7 \text{ ms}^{-1}$ )	Approximately equal to the velocity of light	$3 \times 10^8 \text{ m/s}$
10.	Mutual interaction with matter	Produce heat	Produce heat	Produce the phenomenon of Photoelectric



## 4. SOME BASIC TERMS

### 4.1 Isotopes, Isobars and Isotones :

S.No	Isotopes	Isobars	Isotones
1.	The atoms of the same elements whose charge number (Z) is same but mass number is different are known as isotopes.	The atoms with mass number same and charge number different are known as isobars.	The atoms with same neutron number but A and Z are different are known as isotones
2.	Chemical properties are same	Chemical properties are different	Chemical properties are different
3.	Number of electrons is same	Number of electrons is different	Number of electrons is different
4.	Occupy same place in periodic table	Occupy different places in periodic table	Occupy different places in periodic table.
5.	Example ${}_8\text{O}^{16}$ , ${}_8\text{O}^{17}$ , ${}_8\text{O}^{18}$ ${}_1\text{H}^1$ , ${}_1\text{H}^2$ , ${}_1\text{H}^3$ ${}_{10}\text{Ne}^{20}$ , ${}_{10}\text{Ne}^{21}$ , ${}_{10}\text{Ne}^{22}$	${}_1\text{H}^3$ and ${}_2\text{He}^3$ ${}_6\text{C}^{14}$ and ${}_7\text{N}^{14}$ ${}_8\text{O}^{17}$ and ${}_9\text{F}^{17}$	${}_3\text{Li}^7$ and ${}_4\text{Be}^8$ ${}_1\text{H}^2$ and ${}_2\text{He}^3$ ${}_1\text{H}^3$ and ${}_2\text{He}^4$

### 4.2 Isodiaphers :

Atoms having same isotopic number are called isodiaphers.

Mathematically, isotopic number (isotopic excess) = (N - Z) or (A - 2Z)

Where, N = Number of neutrons; Z = Number of protons

Examples :

(i)  ${}_{92}\text{Np}^{235}$  and  ${}_{90}\text{Th}^{231}$       (ii)  ${}_{19}\text{K}^{39}$  and  ${}_{9}\text{F}^{19}$       (iii)  ${}_{29}\text{Cu}^{65}$  and  ${}_{24}\text{Cr}^{55}$

### 4.3 Isoelectronic species :

Species (atoms, molecules or ions) having same number of electrons are called isoelectronic.

Examples :

(i)  $\text{N}^{3-}$ ,  $\text{O}^{2-}$ ,  $\text{F}^-$ ,  $\text{Ne}$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{CH}_4$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$  and  $\text{HF}$  have 10 electrons each.

(ii)  $\text{P}^{3-}$ ,  $\text{S}^{2-}$ ,  $\text{Cl}^-$ ,  $\text{Ar}$ ,  $\text{K}^+$  and  $\text{Ca}^{2+}$  have 18 electrons each.

(iii)  $\text{H}^-$ ,  $\text{He}$ ,  $\text{Li}^+$  and  $\text{Be}^{2+}$  have 2 electrons each.

(iv)  $\text{CO}$ ,  $\text{CN}^-$  and  $\text{N}_2$  have 14 electrons each.

(v)  $\text{N}_2\text{O}$ ,  $\text{CO}_2$  and  $\text{CNO}^-$  have 22 electrons each.

### 4.4 Isosters :

Molecules having same number of total atoms and also same number of electrons are called isosters.

Examples :

(i)  $\text{N}_2$  and  $\text{CO}$       (ii)  $\text{HCl}$  and  $\text{F}_2$       (iii)  $\text{CaO}$  and  $\text{MgS}$

### Exercise

Match the following :

1. Isotopes

2. Isobars

3. Isosters

4. Isotones

5. Isoelectronic

6. Isodiaphers

A.  ${}_8\text{O}^{16}$  and  ${}_8\text{O}^{17}$

B.  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{F}^-$

C.  ${}_1\text{H}^2$  and  ${}_2\text{He}^3$

D.  $\text{CO}_2$  and  $\text{N}_2\text{O}$

E.  ${}_AX^Z$ ,  ${}_{A-2}X^{Z-2}$

F.  ${}_{20}\text{Ca}^{40}$  and  ${}_{19}\text{K}^{40}$

Ans. 1-A, 2-F, 3-D, 4-C, 5-B, 6-E

## 5. RATE OF RADIOACTIVE DECAY

"According to the law of radioactive decay, the quantity of a radioelement which disappears in unit time (rate of disintegration) is directly proportional to the amount present."

The law of radioactive decay may also be expressed mathematically.

Suppose the number of atoms of the radioactive element present at the commencement of observation, i.e. when  $t = 0$  is  $N_0$ , and after time  $t$ , the number of atoms remaining unchanged is  $N_t$ , then the rate of

decay of atoms is  $-\frac{dN_t}{dt}$  (the word 'd' indicates a very-very small fraction; the negative sign shows that the number of atoms  $N_t$  decreases as time  $t$  increases)

Now since the change in number of atoms is proportional to the total number of atoms  $N_t$ , the relation

becomes  $-\frac{dN_t}{dt} = \lambda N_t$ , where  $\lambda$  is a radioactive constant or decay constant.

Rate of decay of nuclide is **independent** of temperature, so its energy of activation is zero.

Since the rate of decay is directly proportional to the amount of the radioactive nuclide present and as the number of undecomposed atom decreases with increase in time, the rate of decay also decreases with the increase in time. Various forms of equation for radioactive decay are

$$N_t = N_0 e^{-\lambda t};$$

$$\log \frac{N_0}{N_t} = \frac{\lambda t}{2.303}$$

$$\lambda = \frac{2.303}{t} \log \frac{N_0}{N_t}$$

where  $N_0$  = Initial number of atoms of the given nuclide, i.e. at time 0

$N_t$  = Number of atoms of that nuclide present after time  $t$ .

$\lambda$  = Decay constant

**Note :** This equation is similar to that of first order reaction, hence we can say that radioactive disintegration are examples of first order reactions. However, unlike first order rate constant ( $K$ ), the decay constant ( $\lambda$ ) is independent of temperature.

### 5.1 Characteristics of decay constant ( $\lambda$ ) :

It is characteristic of a nuclide (not for an element).

Its units are  $\text{time}^{-1}$ .

Its value is always less than one.

### 5.2 Half-life Period ( $t_{1/2}$ ) :

Rutherford in 1904 introduced a constant known as half-life period of the radio-element for evaluating its radioactivity or for comparing its radioactivity with the activities of other radio-elements. The half-life period of a radio-element is defined as the time required by a given amount of the element of decay to one-half of its initial value.

$$\text{Mathematically, } t_{1/2} = \frac{0.693}{\lambda}$$

- 5.3 Average Life Period (T) :** Since total decay period of any element is infinity, it is meaningless to use the term total decay period (total life period) for radio elements. Thus the term average life is used which is determined by the following relation.

$$\text{Average life (T)} = \frac{\text{Sum of lives of the nuclei}}{\text{Total number of nuclei}}$$

- 5.4 Relation between average life and half-life :** Average life (T) of an element is the inverse of its decay constant i.e.,  $T = \frac{1}{\lambda}$

Substituting the value of  $\lambda$  in the above equation,  $T = \frac{t_{1/2}}{0.693} = 1.44 t_{1/2}$

Thus, Average life (T) =  $1.44 \times \text{Half-life } (t_{1/2}) = \sqrt{2} \times t_{1/2} = 1.414 t_{1/2}$

Thus the average life period of a radioisotope is approximately under-root two times of its half life period.

- 5.5 Specific activity :** It is the measure of radioactivity of a radioactive substance. It is defined as 'the number of radioactive nuclei which decay per second per gram of radioactive isotope'. Mathematically, if 'm' is the mass of radioactive isotope, then

$$\text{Specific activity} = \frac{\text{Rate of decay}}{m} = \frac{\lambda N}{m} = \lambda \times \frac{\text{Avogadro number}}{\text{Atomic mass in g}}$$

Where N is the number of radioactive nuclei, which undergoes disintegration.

## 5.6 Activity (A) :

- The number of atoms of any material decaying per second is defined as the activity of that material.
- Its value depends on the quantity and nature of that material.
- Formulae of activity

$$(i) A = -\frac{dN}{dt} \quad (ii) A = \lambda N$$

$$(iii) A_0 = \lambda N_0 \quad (iv) A = A_0 e^{-\lambda t}$$

where  $A_0$  = maximum initial activity; A = activity after time t,  $\lambda$  = decay constant,

$N_A$  = Avogadro number,

m = mass of material

## 5.7 Units of Radioactivity –

S.I unit – disintegrations per second i.e., Bq

1 Bq = 1 disintegration/s

Practical units: curie and rutherford.

1 curie =  $3.7 \times 10^{10}$  disintegration/second:

1 Rutherford =  $10^6$  disintegrations/second.



**Illustration :**

1. The half life period of  $_{53}\text{I}^{125}$  is 60 day. What % of radioactivity would be present after 180 day?

**Sol.**  $t_{1/2} = 60$  day,  $T = 180$  day

$$\therefore n = \frac{T}{t_{1/2}} = \frac{180}{60} = 3$$

$$\therefore \% \text{ of radioactivity left after 3 halves} = \frac{N_0}{2^3} = \frac{100}{2^3} = 12.5\%$$

2. What mass of  $^{14}\text{C}$  isotope will have an activity equal to one curie?  $t_{1/2}$  of  $^{14}\text{C}$  is 5730 years.

**Sol.**  $-\frac{dN}{dt} = 1 \text{ curie} = 3.7 \times 10^{10} \text{ disintegrations per second}$

$$\lambda = \frac{0.693}{5730 \times 365 \times 24 \times 3600}$$

$$-\frac{dN}{dt} = \lambda N \text{ or } 3.7 \times 10^{10} = \frac{0.693}{5730 \times 365 \times 24 \times 3600} \times N$$

$$\text{Or } N = 9.65 \times 10^{21} \text{ atoms}$$

$$\text{Or amount of } ^{14}\text{C} = \frac{14}{6.023 \times 10^{23}} \times 9.65 \times 10^{21} = 0.2244 \text{ g}$$

**Exercise**

1. The half-life period of a radio active element is 100 seconds. Calculate the disintegration constant and average life period. How much time will it take for 90% decay?

**Ans.**  $0.00693 \text{ s}^{-1}$ , 144.3 s, 332.3 s

**6. THEORY OF RADIOACTIVE DISINTEGRATION**

**Rutherford and Soddy**, in 1903, postulated that radioactivity is a nuclear phenomenon and all the radioactive changes are taking place in the nucleus of the atom. They presented an interpretation of the radioactive processes and the origin of radiations in the form of a theory known as **theory of radioactive disintegration**. The main points of this theory are as follows :

The atomic nuclei of the radioactive elements are unstable and liable to disintegrate any moment.

The disintegration is spontaneous, i.e., constantly breaking. The rate of breaking is not affected by external factors like temperature, pressure, chemical combination etc.

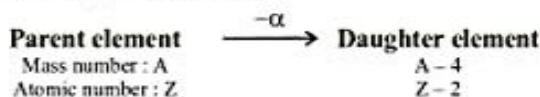
During disintegration, atoms of new elements called daughter elements having different physical and chemical properties than the parent elements come into existence.

During disintegration, either alpha or beta particles are emitted from the nucleus.

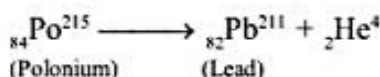
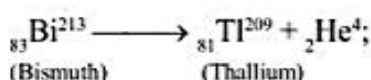
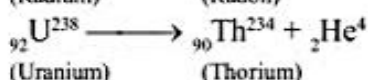
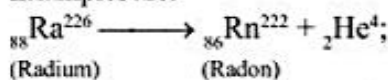


The disintegration process may proceed in one of the following two ways :

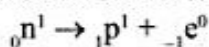
- 6.1  $\alpha$ -particle emission :** When an  $\alpha$ -particle ( ${}_2\text{He}^4$ ) is emitted from the nucleus of an atom of the parent element, the nucleus of the new element, called daughter element possesses atomic mass or atomic mass number less by four units and nuclear charge or atomic number less by 2 units because  $\alpha$ -particle has mass of 4 units and nuclear charge of two units.



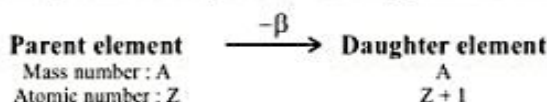
Examples are:



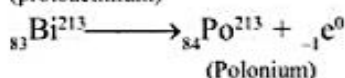
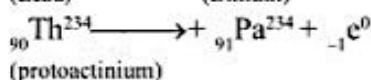
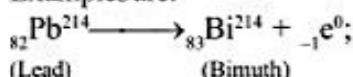
- 6.2  $\beta$ -particle emission :**  $\beta$ -particle is merely an electron which has negligible mass. Whenever a beta particle is emitted from the nucleus of a radioactive atom, the nucleus of the new element formed possesses the same atomic mass but nuclear charge or atomic number is increased by 1 unit than the parent element. Beta particle emission is due to the result of decay of neutron into proton and electron.



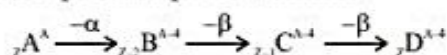
The electron produced escapes as a beta-particle-leaving proton in the nucleus.



Examples are:



**Special case :** If in a radioactive transformation 1 alpha and 2 beta-particles are emitted, the resulting nucleus possesses the same atomic number but atomic mass is less by 4 units. A radioactive transformation of this type always produces an isotope of the parent element.



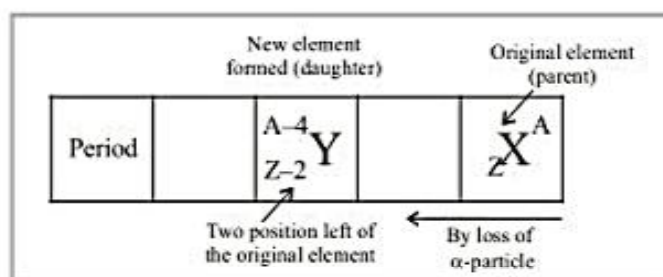
A and D are isotopes.

- 6.3  $\gamma$ -rays emission :**  $\gamma$ -rays are emitted due to secondary effects. The excess of energy is released in the form of  $\gamma$ -rays. Thus  $\gamma$ -rays arise from energy re-arrangements in the nucleus. As  $\gamma$ -rays are short wavelength electromagnetic radiations with no charge and no mass, their emission from a radioactive element does not produce new element.

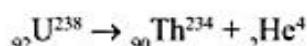
## 7. GROUP DISPLACEMENT LAW

Soddy, Fajans and Russell (1911-1913) observed that when an  $\alpha$ -particle is lost, a new element with atomic number less by 2 and mass number less by 4 is formed. Similarly, when  $\beta$ -particle is lost, new element with atomic number greater by 1 is obtained. The element emitting then  $\alpha$  or  $\beta$ -particle is called parent element and the new element formed is called daughter element. The above results have been summarized as **Group displacement laws** as follows :

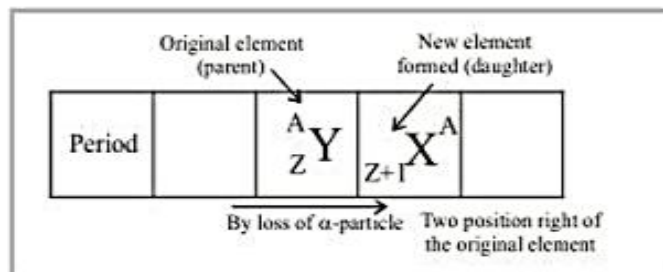
- (1) When an  $\alpha$ -particle is emitted, the new element formed is displaced two positions to the **left** in the periodic table than that of the parent element (because the atomic number decreases by 2).



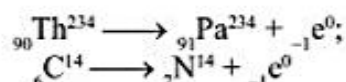
For example, when



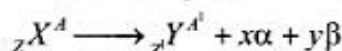
- (2) When a  $\beta$ -particle is emitted, the new element formed is displaced one position to the **right** in the periodic table than that of the parent element (because atomic number increased by 1).



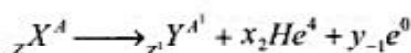
For example,



### 7.1 To calculate no of $\alpha$ -particles and $\beta$ -particle emitted

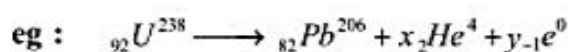


x: no of  $\alpha$ -particles emitted    y: no of  $\beta$ -particles emitted



$$A = A' + 4x \qquad x = \frac{A - A'}{4}$$

$$Z = Z' + 2x - y \qquad y = Z' - Z + 2x \qquad y = \left( \frac{A - A'}{2} \right) - (Z - Z')$$



$$x = \frac{A - A'}{4} = \frac{238 - 206}{4} = 8,$$

no. of  $\alpha$ -particles = 8

$$y = \left( \frac{A - A'}{2} \right) - (Z - Z') = \left( \frac{238 - 206}{2} \right) - (92 - 82) = 16 - 10 = 6,$$

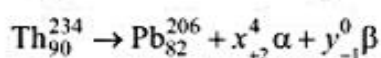
no. of  $\beta$ -particles = 6

### Illustration :

1.  $\text{Th}_{90}^{234}$  disintegrates to give  $\text{Pb}_{82}^{206}$  as the final product.  $\alpha$  and  $\beta$  particles emitted during the process are  
 (A) 7 and 6 (B) 6 and 7 (C) 2 and 4 (D) 4 and 2

Ans. (A)

Sol. Suppose the number of  $\alpha$  particles emitted are 'x' and  $\beta$  particles emitted are 'y'. Then,



On equating mass number on both sides, we obtain

$$234 = 206 + 4x + 0y$$

$$\text{Or } x = 7$$

On equating atomic number on both sides,

$$90 = 82 + 2x - y = 82 + 2 \cdot 7 - y$$

$$\text{Or } y = 6$$

So, 7 $\alpha$  and 6 $\beta$  particles are emitted.

### Exercise :

The mass number of Th is 232 and its atomic number is 90. In terms of its radioactive disintegration six  $\alpha$  and four  $\beta$ -particles are emitted. What is mass no. and at. no. of products ?

Ans. 208, 82

## 8. THEORIES REGARDING NUCLEAR STABILITY

### 8.1 Even odd theory of nuclear stability

The number of stable nuclides is maximum when both p and n are even number.

p	n	No. of stable nucleus
even	even	165
even	odd	55
odd	even	50
odd	odd	5

### 8.2 Magic numbers and nuclear stability

Nuclei with 2, 8, 20, 28, 50, 82 or 126 protons or neutrons are exceptionally stable and have a larger number of stable isotopes than neighboring nuclei in the periodic table. These numbers are called magic numbers. They are supposed to represent completely filled nuclear shells of energy levels.

e.g.  $_{50}\text{Sn}$  having 10 stable isotopes while  $_{51}\text{Sb}$  has only two stable isotopes.



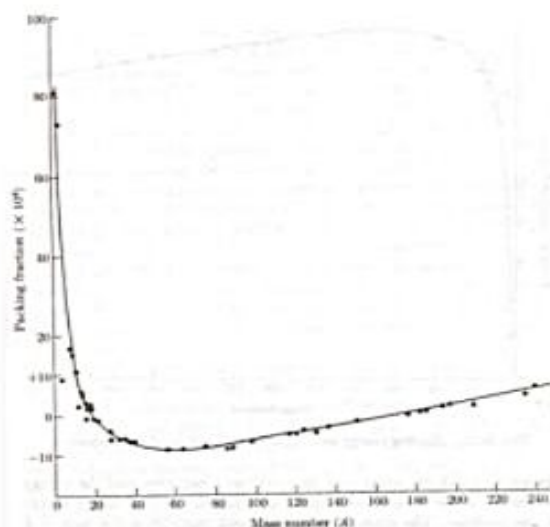
Nuclei with magic number of protons as well as neutrons have notably high stabilities. [eg.  ${}^4_2\text{He}$ ,  ${}^{16}_8\text{O}$ ,  ${}^{40}_{20}\text{Ca}$  and  ${}^{208}_{82}\text{Pb}$ ]. 165 such stable nuclei are known.

### 8.3 Packing Fraction

'Aston' expressed relation between isotopic mass & mass number in terms of packing fraction.

$$\text{Packing Fraction} = \frac{\text{Atomic mass} - \text{Mass number}}{\text{Mass number}} \times 10^4$$

Packing fraction of C-12 is exactly zero. packing fraction may be positive or negative. Negative packing fraction implies that nuclei is stable. Positive packing fraction implies that nuclei is unstable. Some lighter nuclei have positive packing fraction although nucleus is stable. Mo, Ru, Rh, Pd have lowest packing fraction



### 8.4 Binding Energy : It is defined energy required to break the nucleus into its component protons & neutrons. Binding energy per nucleon gives a quantitative measure of nuclear stability.

Mass defect ( $\Delta m$ ) = mass of neutron + mass of proton – mass of nucleus

Binding energy of nucleus =  $\Delta m c^2$

The binding energy for a nucleus containing Z protons and N neutrons can be calculated as

$$\text{Binding energy} = (ZM_H + Nm_n - {}^A_ZM)c^2$$

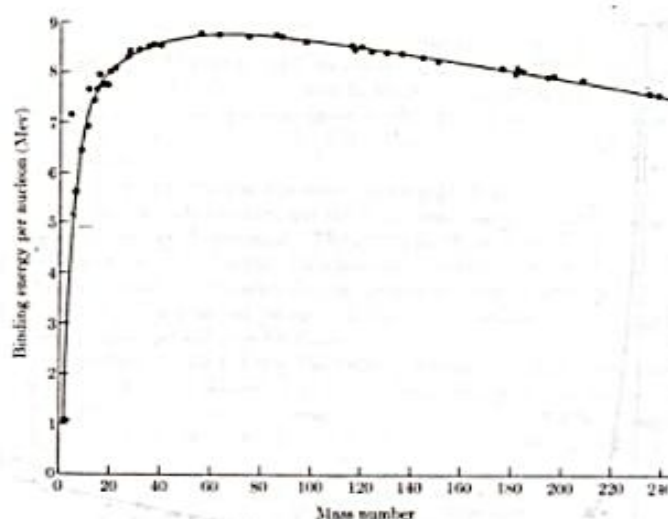
Note that above equation does not include  $Zm_p$ , the mass of Z protons. Rather, it contains  $ZM_H$ , the mass of Z protons and Z electrons combined as Z neutral  ${}^1_1\text{H}$  atoms, to balance the Z electrons included in  ${}^A_ZM$ , the mass of the neutral atom.

If  $\Delta m = 1 \text{ a.m.u}$  then B.E. = 931.5 MeV

$$\text{B.E. per nucleon} = \frac{\text{B.E.}}{\text{No. of nucleons}}$$

- \* A very heavy nucleus, say  $A = 240$ , has lower binding energy per nucleon compared to that of a nucleus with  $A = 120$ . Thus if a nucleus  $A = 240$  breaks into two  $A = 120$  nuclei, energy would be released in the process. This implies nucleons get more tightly bound. It has very important applications for energy production through fission.





- \* Consider two very light nuclei ( $A \leq 10$ ) joining to form a heavier nucleus. The binding energy per nucleon of the heavier nuclei is more than the binding energy per nucleon of the lighter nuclei, again energy would be released in such a process of fusion. Nuclear binding energy is maximum for mass number 50 – 60. Fe, Co, Ni very high nuclear binding energy.

### Illustration :

1. The atomic mass of  ${}^8_{16}\text{O} = 15.9949$  amu. Calculate the BE/nucleon for this atom. Mass of  $1n$  and  $1p$  is  $2.016490$  amu. and  $m_e = 0.00055$  amu.

Sol. Mass of  $1n + 1p = 2.016490$  amu.

$$\therefore \text{Mass of } 8n + 8p = 8 \times (2.016490) \text{ amu.}$$

$$\therefore \text{Total mass of } {}^{16}\text{O} \text{ atom} = m(p+n) + m(\text{electron}) \quad (m = \text{mass})$$

$$= 8 \times (2.016490) + 0.00055 \times 8 = 16.13632 \text{ amu}$$

$$\therefore \text{Mass defect} = 16.1363 - 15.9949 = 0.1414 \text{ amu}$$

$$\therefore \text{BE} = \text{Mass defect} \times 931.478 \text{ MeV}$$

$$= 0.1414 \times 931.487 = 131.71 \text{ MeV}$$

$$\therefore \text{BE/nucleon} = \frac{\text{Total BE}}{\text{No. of nucleons}} = \frac{131.71}{16} = 8.232 \text{ MeV}$$

2. Calculate the mass defect and binding energy per nucleon for an alpha particle whose mass is  $4.0028$  amu.  $m_p = 1.0073$  and  $m_n = 1.0087$  amu.

Sol.  $\alpha$ -particle has  $2p$  and  $2n$

$$\therefore \text{Mass of } 2p + 2n \text{ in } \alpha\text{-particle} = (2 \times 1.0073) + (2 \times 1.0087) = 4.032 \text{ amu}$$

$$\text{Actual mass of } \alpha\text{-particle (given)} = 4.0028 \text{ amu}$$

$$\therefore \text{Mass defect} = 4.032 - 4.0028 = 0.0292 \text{ amu.}$$

$$\text{Now BE} = \text{Mass defect} \times 931 = 0.0292 \times 931 = 27.1852 \text{ MeV}$$

$$\therefore \text{BE/Nucleon} = \frac{27.1852}{4} = 6.7963 \text{ MeV}$$

**Exercise :**

1. Calculate the binding energy for  ${}_1\text{H}^2$  atom. The mass of  ${}_1\text{H}^2$  atom is 2.014102 amu, where  $1n$  and  $1p$  have their weights 2.016490 amu. Neglect mass of electron.

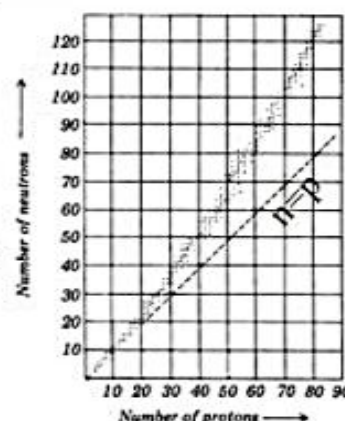
Ans. 2.2232 MeV

### 8.5 Neutron / proton ratio and stability belt

For atomic number  $< 20$ , most stable nuclei have  $n : p$  ratio nearly 1 : 1 (except H & Ar).

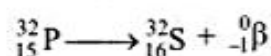
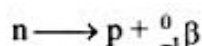
For  $n/p$  ratio  $> 1.52$ , nucleus is unstable. Largest stable nucleus is  ${}_{83}^{209}\text{Bi}$  for which  $n/p$  ratio is 1.52.

For atomic number  $> 83$ , there are no stable nuclei.



## 9. EXPECTED EMISSIONS FROM UNSTABLE NUCLEUS

- 9.1  **$n/p$  ratio above stability belt :** Those nucleus which have high value of  $n/p$  ratio (lie above the stability belt) undergoes  ${}_{-1}^0\beta$  decay.



Beta decay is possible whenever the mass of the original neutral atom is greater than the final atom.

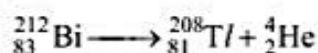
The difference between the rest mass energy of the initial constituents and that of the final products is called the  $Q$ -value of the process. Thus, if  $U_i$  is the rest mass energy of the initial constituents and  $U_f$  is that of the final products,

$$Q = U_i - U_f$$

$Q$  value is positive i.e. isolated neutron may decay into proton. The energy of  ${}_{-1}^0\beta$  particle can be any thing between zero &  $Q$ . Such transformation takes place because of weak forces operating within the nucleus.

- 9.2  **$n/p$  ratio below stability belt :**

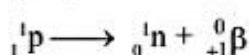
(a)  **$\alpha$ -decay**



Observed in nuclei with  $A > 210$

Mass number & the atomic number of the daughter nucleus decreases by 4 & 2 respectively compared to parent nucleus. Alpha decay may take place spontaneously or it can be initiated. Alpha decay is possible whenever the mass of the original neutral atom is greater than the sum of the masses of the final neutral atom and the neutral helium-4 atom. All the alpha particles coming from a particular decay reaction have the same kinetic energy.

- (b)  **$({}_{+1}^0\beta)$  Positron decay**

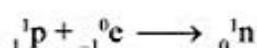
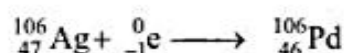
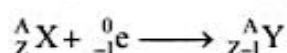


Those nucleus which have low value of n/p ratio (lie below the stability belt) undergoes  ${}^0_{+1}\beta$  decay.

Q value is negative i.e. isolated proton will not decay into neutron.

Positron decay is possible whenever the mass of the original neutral atom is greater than at least two electron masses larger than the final atom.

- (c) **K electron capture** - Electron is captured from 1st shell and one neutron is formed by the combination of captured  $e^-$  and a proton of the nucleus.



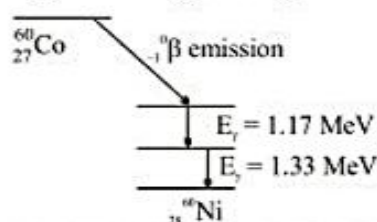
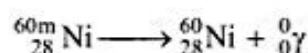
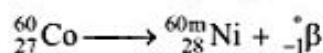
\* Electron capture can occur when ever the mass of original neutral atom is larger than that of final atom.

\* Those nucleus having low n/p ratio can capture K shell electron.

\* X-rays are emitted during the process.

- (d)  **$\gamma$ -decay**

When an  $\alpha$  or  $\beta$  decay takes place, the daughter nucleus generally formed is in excited state & comes to ground state by a single or successive transitions by emitting electromagnetic radiations i.e.  $\gamma$  rays.



No. of neutron and proton is unchanged while quantum state of nucleon changes.

## 10. RADIOACTIVE DISINTEGRATION SERIES

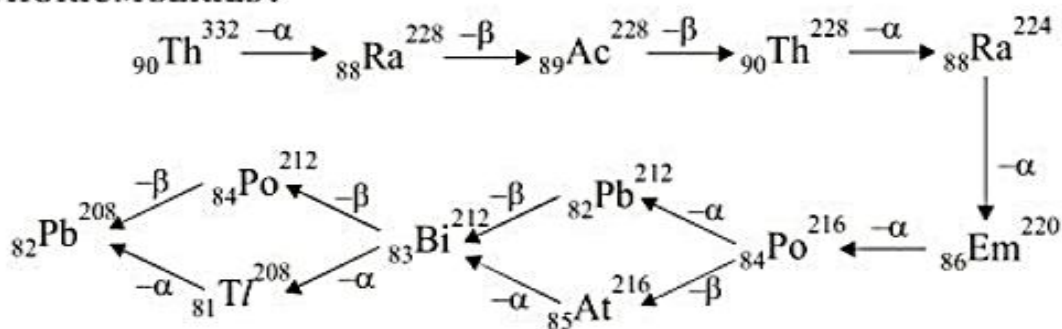
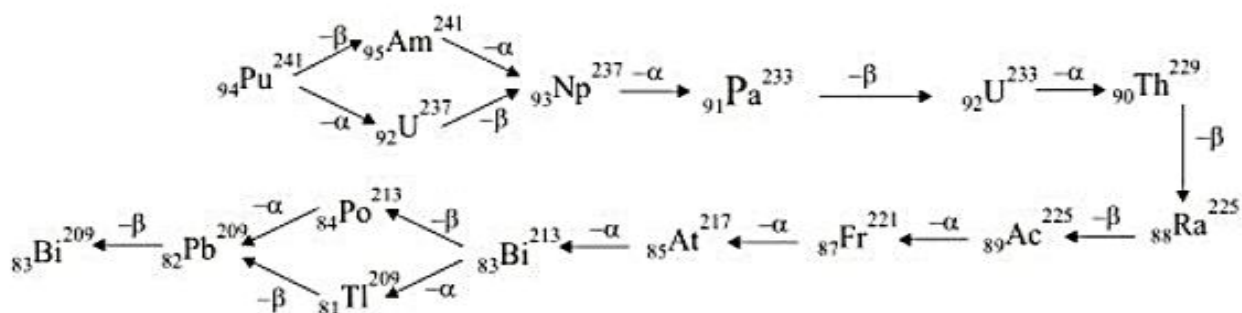
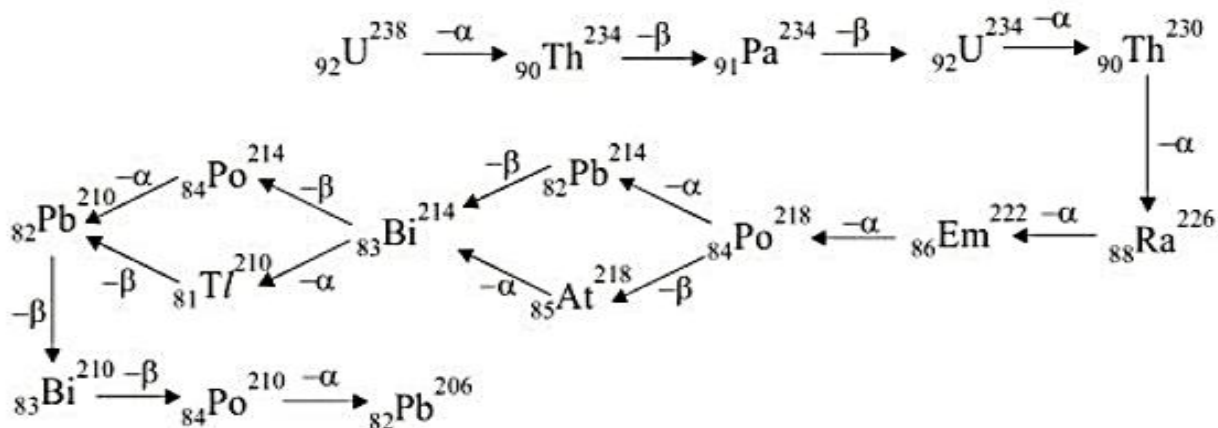
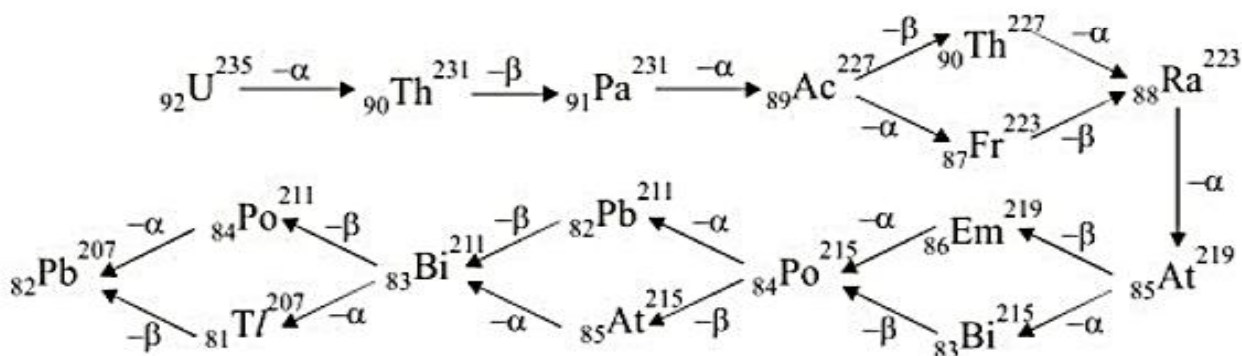
Many radioactive nucleus ( $Z > 82$ ) are obtained in nature as a member of natural decay series.

The series of nuclear reaction is known as radioactive disintegration series.

Series	Parent Nucleus	Last Nucleus	No. of $\alpha$	No. of $\beta$
4n or Thorium series	$\text{Th}^{232}$	$\text{Pb}^{208}$	6	4
(4n+1) or Neptunium series	$\text{Pu}^{241}$	$\text{Bi}^{209}$	8	5
4n+2 or Uranium series	$\text{U}^{238}$	$\text{Pb}^{206}$	8	6
4n+3 or Actinium series	$\text{U}^{235}$	$\text{Pb}^{207}$	7	4

4n, 4n + 2 and 4n + 3 series are natural while (4n + 1) is artificial.



**THE THORIUM SERIES :****THE NEPTUNIUM SERIES :****THE URANIUM SERIES :****THE ACTINIUM SERIES :**



## 11. APPLICATION OF RADIOACTIVITY

Radioisotopes find numerous applications in a variety of areas such as medicine, agriculture, biology, chemistry, archeology, engineering and industry. Some of the are given below :

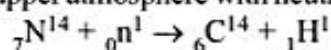
- 11.1 Age determination (carbon dating) :** Radioactive decay follows a very exact law, and is virtually unaffected by heat, pressure, or the state of chemical combination of the decaying nuclei, it can be used as a very precise clock for dating past events. For instance, the age of earth has been determined by uranium dating technique as follows. Samples of uranium ores are found to contain  $\text{Pb}^{206}$  as a result of long series of  $\alpha$ - and  $\beta$ -decays. Now if it is assumed that the ore sample contained no lead at the moment of its formation, and if none of the lead formed from  $\text{U}^{238}$  decay has been lost then the measurement of the  $\text{Pb}^{206}/\text{U}^{238}$  ratio will give the value of time  $t$  of the mineral.

$$\frac{\text{No. of atoms of } \text{Pb}^{206}}{\text{No. of atoms of } \text{U}^{238} \text{ left}} = e^{-\lambda t - 1}, \text{ where } \lambda \text{ is the decay constant of uranium-238}$$

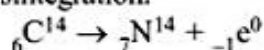
$$\text{Alternatively, } t = \frac{2.303}{\lambda} \log \frac{\text{Initial amount of } \text{U}^{238}}{\text{Amount of } \text{U}^{238} \text{ in the mineral present till date}}$$

Similarly, the less abundant isotope of uranium,  $\text{U}^{235}$  eventually decays to  $\text{Pb}^{207}$ ;  $\text{Th}^{232}$  decays to  $\text{Pb}^{208}$  and thus the ratios of  $\text{Pb}^{207}/\text{U}^{235}$  and  $\text{Pb}^{208}/\text{Th}^{232}$  can be used to determine the age of rocks and minerals. Many ages have been determined by this way to give result from hundreds to thousands of million of years.

Besides the above long-lived radioactive substances viz.  $\text{U}^{238}$ ,  $\text{U}^{235}$  and  $\text{Th}^{232}$  (which have been present on earth since the elements were formed), several short-lived radioactive species have been used to determine the age of wood or animal fossils. One of the most interesting substances is  ${}^6_6\text{C}^{14}$  (half-life 5760 years) which was used by **Willard Libby** (Nobel lauret) in determining the age of carbon-bearing materials (e.g. wood, animal fossils, etc.) Carbon-14 is produced by the bombardment of nitrogen atoms present in the upper atmosphere with neutrons (from cosmic rays).



Thus carbon-14 is oxidised to  $\text{CO}_2$  and eventually ingested by plants and animals. The death of plants or animals puts an end to the intake of  $\text{C}^{14}$  from the atmosphere. After this the amount of  $\text{C}^{14}$  in the dead tissues starts decreasing due to its disintegration.



It has been observed that on an average, one gram of radioactive carbon emits about 12  $\beta$ -particles per minute. Thus by knowing either the amount of C-14 or the number of  $\beta$ -particles emitted per minute per gram of carbon at the initial and final (present) stages, the age of carbon material can be determined by using the following formulae.

$$\lambda = \frac{2.303}{t} \log \frac{N_0}{N_t} \text{ or } t = \frac{2.303}{\lambda} \log \frac{N_0}{N_t}$$

where  $t$  = Age of the fossil,  $\lambda$  = Decay constant,  $N_0$  = Initial radioactivity (in the fresh wood),  $N_t$  = Radioactivity in the fossil

The above formula can be modified as

$$t = \frac{2.303}{\lambda} \log \frac{\text{Initial of } \text{C}^{14} / \text{C}^{12} \text{ (in fresh wood)}}{\text{C}^{14} / \text{C}^{12} \text{ ratio in the old wood}}$$

$$\begin{aligned}
 &= \frac{2.303}{\lambda} \log \frac{\text{Initial amount of } C^{14} / C^{12} \text{ (in fresh wood)}}{\text{Amount of } C^{14} \text{ in the old wood}} \\
 &= \frac{2.303}{\lambda} \log \frac{\text{Radioactivity in fresh wood due to } C^{14}}{\text{Radioactivity in old wood due to } C^{14}} \\
 &= \frac{2.303 \times t_{1/2} \text{ of } C^{14}}{0.693} \log \frac{\text{counts min}^{-1} \text{ g}^{-1} \text{ of } C^{14} \text{ in fresh wood}}{\text{counts min}^{-1} \text{ g}^{-1} \text{ of } C^{14} \text{ in old wood}}
 \end{aligned}$$

Similarly, tritium  ${}^3_1\text{H}$  has been used for dating purposes.

### Illustration :

1. An old piece of wood has 25.6% as much  $C^{14}$  as ordinary wood today has.  $t_{1/2}$  of  $C^{14}$  is 5760 years. Calculate the age of the wood?

**Sol.** 'a' = amount of  $C^{14}$  present originally in wood

$$\text{Amount of } C^{14} \text{ now present in old wood} = (a - x) = \frac{25.6}{100} a = 0.256a$$

$\therefore$  time 't' in which 'a' has changed to 0.256 a is

$$t = \frac{2.303}{\lambda} \log \frac{a}{0.256 a}$$

$$\text{Now, } \lambda = 0.693/5760 = 1.203 \times 10^{-4} \text{ y}^{-1}$$

$$t = \frac{2.303}{1.203 \times 10^{-4}} \log \frac{1}{0.256} \Rightarrow t = 11329 \text{ years}$$

### Exercise :

1. The  ${}_6C^{14}$  and  ${}_6C^{12}$  ratio in a piece of wood is 1/16 part that of atmosphere. Calculate the age of wood. ( $t_{1/2}$  of  $C^{14}$  is 5577 year).

**Ans.** 22308 year

**11.2 Radioactive tracers (use of radio-isotopes) :** A radioactive isotope can be easily identified by its radioactivity. Because of similar physical and chemical properties of radioisotopes and non-radioisotopes of an element, if a small quantity of the former is mixed with normal isotope, then chemical reactions can be studied by determining the radioactivity of the radioisotope. The radioactivity can, therefore act as a tag or label that allows studying the behaviour of the element or compounding which contains this isotope. An isotope added for this purpose is known as isotopic tracer. The radioactive tracer is also known as an isotopic tracer. The radioactive tracer is also known as an indicator because it indicates the reaction. Radioisotopes of moderate half-life periods are used for tracer work. The activity of radioisotopes can be detected by means of electroscope, the electrometer or the Geiger-Muller counter. Tracers have been used in the following fields :



**(i) In medicine :** Radioisotopes are used to diagnose many diseases. For example, Arsenic - 74 tracer is used to detect the presence of tumours, Sodium -24 tracer is used to detect the presence of blood clots and Iodine -131 tracer is used to study the activity of the thyroid gland. It should be noted that the radioactive isotopes used in medicine have very short half-life periods.

**(ii) In agriculture :** The use of radioactive phosphorus  $^{32}\text{P}$  in fertilizers has revealed how phosphorus is absorbed by plants. This study has led to an improvement in the preparation of fertilizers.  $^{14}\text{C}$  is used to study the kinetics of photo synthesis.

**(iii) In industry :** Radioisotopes are used in industry to detect the leakage in underground oil pipelines, gas pipelines and water pipes. Radioactive isotopes are used to measure the thickness of materials, to test the wear and tear inside a car engine and the effectiveness of various lubricants. Radioactive carbon has been used as a tracer in studying mechanisms involved in many reactions of industrial importance such as alkylation, polymerization, catalytic synthesis etc.

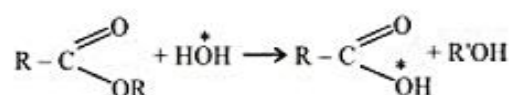
**(iv) Analytical Studies :** Several analytical procedures can be used employing radioisotopes as tracers.

**(a) Adsorption and occlusion studies :** A small amount of radioactive isotope is mixed with the inactive substance and the activity is studied before and after adsorption. Fall in activity gives the amount of substance adsorbed.

**(b) Solubility of sparingly soluble salt :** The solubility of lead sulphate in water may be estimated by mixing a known amount of radioactive lead with ordinary lead. This is dissolved in nitric acid and precipitate as lead sulphate by adding sulphuric acid. Insoluble lead sulphate is filtered and the activity of the water is measured. From this, the amount of  $\text{PbSO}_4$  still present in water can be estimated.

**(c) Ion-exchange technique :** Ion exchange process of separation is readily followed by measuring activity of successive fractions eluted from the column.

**(d) Reaction mechanism :** By labelling oxygen of the water, mechanism of ester hydrolysis has been studied.



**(e) Study of efficiency of analytical separations :** The efficiency of analytical procedures may be measured by adding a known amount of radio-isotopes to the sample before analysis begins. After the completion, the activity is again determined. The comparison of activity tells about the efficiency of separation.

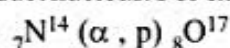
- 11.3 Use of  $\gamma$ -rays :**  $\gamma$ -rays are used for disinfecting food grains and for preserving food stuffs. Onions, potatoes, fruits and fish etc., when irradiated with  $\gamma$ -rays, can be preserved for long periods. High yielding disease resistant varieties of wheat, rice, groundnut, jute etc., can be developed by the application of nuclear radiations. The  $\gamma$ -rays radiations are used in the treatment of cancer. The radiations emitted by cobalt -60 can burn cancerous cells. The  $\gamma$ -radiations are used to sterilize medical instruments like syringes, blood transfusion sets. etc. These radiations make the rubber and plastics objects heat resistant.

## 12. NUCLEAR REACTIONS

The reactions in which nuclei of atoms interact with other nuclei or elementary particles such as  $\alpha$ -particle, proton, neutron, deuteron, etc, resulting in the formation of new nuclei with or without liberation of one or more elementary particles, are called nuclear reactions. The particles resulting nuclear reactions are also called projectiles. In all the nuclear reactions, the total number of protons and neutrons are conserved. Nuclear reactions may be expressed as similar as chemical reactions, like



Here, the nucleus of nitrogen atom is converted in to the nucleus of oxygen atom by a-particle and proton is also produced as a by-product. These reactions may be expressed by short hand notation, in which the projectile and the liberating particle are expressed by their symbols, in a small bracket in between the parent and the product nucleus. For example, the above reaction may also be expressed as:

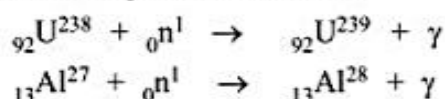


### 12.1 Some differences between nuclear and chemical reactions

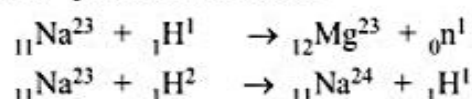
No.	Chemical reaction	Nuclear reaction
1.	No new element is formed	New element is formed
2.	Valence electrons of atoms participates	Only the nucleus of atoms participates
3.	Balanced by the conservation of atoms	Balanced by the conservation of nuclear charge and mass number (total number of neutrons and protons)
4.	Mass conservation is obeyed	Disobey mass conservation
5.	May be exothermic or endothermic, liberating or absorbing relatively small amount of energy	May be exothermic or endothermic, liberating or absorbing relatively very high amount of energy
6.	May be reversible	Irreversible
7.	May obey kinetics of any order	Obeys only first order kinetics
8.	Rate depends on external factors like temperature and the catalytic conditions	Rate is independent from any external condition

### 12.2 Types of Nuclear Reactions :

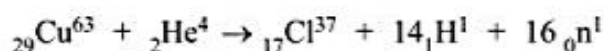
#### (i) Projectile Capture Reactions:



#### (ii) Particle - particle reactions:



#### (iii) Spallation reactions: High speed projectiles with 400Mev bombarded on high nucleus giving smaller nucleus.

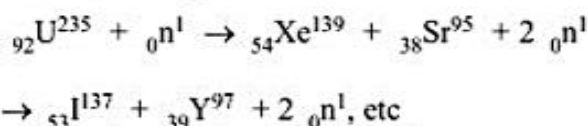




- (iv) **Fission reactions:** It is the nuclear reaction in which a heavy nucleus is broken down by a slow or thermal neutron (energy about 0.04 eV) into two relatively smaller nuclei with the emission of two or more neutrons and large amount of energy. For example,

the reaction of atom bomb:  ${}_{92}\text{U}^{235} + {}_0\text{n}^1 \rightarrow {}_{56}\text{Ba}^{141} + {}_{36}\text{Kr}^{92} + 3 {}_0\text{n}^1 + 200 \text{ MeV}$

It is also found that the products of nuclear fission reactions are not unique. Some more products are formed. The most probable mass numbers of the two nuclides formed are around 95 and 140 and an average of 2.5 neutrons is emitted out per fission.



The destructive action of atom bomb is due to the following reasons:

- (a) As some neutrons are produced in each fission, they may collide efficiently with the other  $\text{U}^{235}$  nuclei to produce more neutrons and thus the reaction occurs in chain like fashion. It results the emission of a large amount of energy in very small time.
- (b) Each product of fission is radioactive and hence increases the intensity of radiation in that region, resulting the problems due to radiations.
- (v) **Fusion reactions:** It is the nuclear reaction in which two or more light nuclei fused together to form heavier nuclei, with the evolution of tremendous amount of energy. In such reactions, relatively more stable nucleus having higher binding energy per nucleon is formed. Such reaction is difficult to occur because when the nuclei of different atoms come closer, they repel each other strongly. This is why, very high temperature of the order  $10^6\text{K}$  is needed for the occurrence of such reactions. However, the overall reaction is highly exothermic due to large mass defect. Some examples of nuclear fusion reactions are:

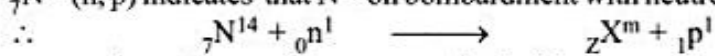
**Probable reaction occurring at the surface of sun:**  $4 {}_1\text{H}^1 \rightarrow {}_2\text{He}^4 + 2 {}_{+1}\text{e}^0 + 24.7 \text{ MeV}$

### Illustration :

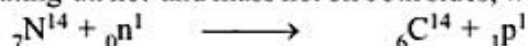
Write equations for the following transformations :

- (a)  ${}_7\text{N}^{14}$  (n, p)      (b)  ${}_{19}\text{K}^{39}$  (p,  $\alpha$ )      (c)  $\beta^+$ -decay by  ${}_{11}\text{Na}^{22}$

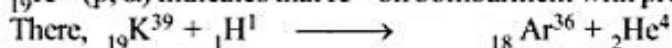
**Sol.** (a)  ${}_7\text{N}^{14}$  (n, p) indicates that  $\text{N}^{14}$  on bombardment with neutrons gives proton.



on equating at. no. and mass no. on both sides, we get



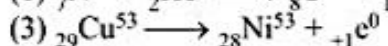
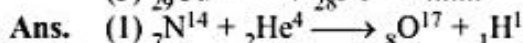
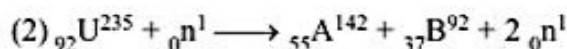
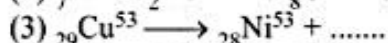
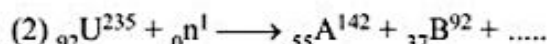
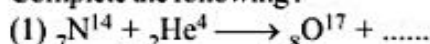
- (b)  ${}_{19}\text{K}^{39}$  (p,  $\alpha$ ) indicates that  $\text{K}^{39}$  on bombardment with proton gives  $\alpha$ -particle.



- (c)  ${}_{11}\text{Na}^{22} \longrightarrow {}_{10}\text{Ne}^{22} + {}_{+1}\text{e}^0$  ( $\beta^+$  or positron)

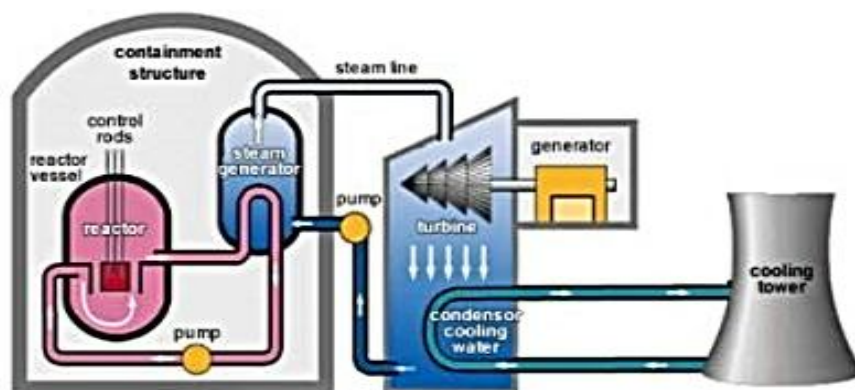
### Exercise :

Complete the following :

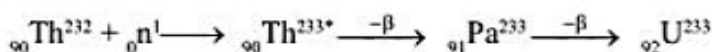
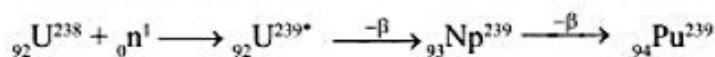


### 13. NUCLEAR REACTOR

A nuclear reactor is the furnace, place where nuclear fission reaction is performed to get energy. The essentials of a nuclear reactor are:



- (i) **Fuel** : Nuclear fuels are of two types:
- (a) **Fissile materials** : These are the nuclides which directly results chain reaction on bombardment with slow neutrons. Such nuclides are  $U^{235}$ ,  $Pu^{239}$ ,  $U^{233}$ , etc.
- (b) **Fertile material** : These are the nuclides which are non-fissile, but they may be converted in to a fissile material by the action of neutrons. Such nuclides are  $U^{238}$  and  $Th^{232}$ .



Such conversions are performed in a special type of nuclear reactor called Breeder Reactor.

- (ii) **Moderator**: It is used to slow down the fast neutrons without absorbing them. Example: water, graphite, helium,  $D_2O$  etc.
- (iii) **Control rods**: These are the rods of material which can absorb neutrons and hence control the fission reaction. Example: Cadmium, boron, etc.
- (iv) **Coolant**: These are the material which transforms the energy produced in the fission reaction in to heat energy. Example: Liquid alloy of sodium and potassium, heavy water, polyphenyls, etc

### 14. ARTIFICIAL TRANSMUTATION

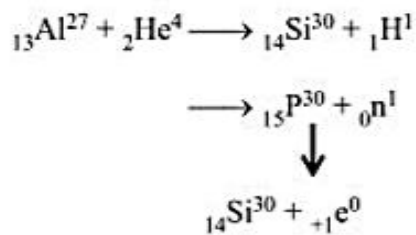
It is the method of conversion of atom of one element in to the atom of other element with the help of some particles like alpha particle, proton, deuteron, neutron, etc (called projectiles). The first such transmutation was performed by Rutherford. When  $N^{14}$  atoms were bombarded by very fast moving  $\alpha$ -particles, the nitrogen atom has changed in to oxygen atom and proton is produced simultaneously



Later on, Rutherford and Chadwick shown that most of the nuclei may be transmuted by the suitable projectile. After the discovery of cyclotron, a particle accelerating machine, such transmutations become more easier.

## 15. ARTIFICIAL RADIOACTIVITY

When Irene Curie and F. Joliot bombarded the atoms of  $\text{Al}^{27}$ ,  $\text{B}^{10}$  or  $\text{Mg}^{24}$  by fast moving  $\alpha$ -particles, protons, neutrons and positrons were produced. They observed that the emission of protons and neutrons stop on stopping the bombardment but the emission of positron continues. They also observed that the rate of emission of positron decreases exponentially in the manner similar to natural radioactivity. They named the isotope emitting positron as **artificial radioisotope** and the phenomenon as **artificial radioactivity**.





## SOLVED EXAMPLES

**Q.1** The half-life of a radioisotope is 1.5 hours. If its initial mass is 32 g, the mass left undecayed after 6 hours is

- (A) 32 g (B) 16 g (C) 4 g (D) 2 g

**Ans.** (D)

**Sol.**  $N = \text{mass left} = \frac{N_0 (\text{initial mass})}{2^{t/t_{1/2}}}$

$$N = \frac{32}{2^4} \left( \text{since } t/t_{1/2} = 6/1.5 = 4 \right) = 2 \text{ g}$$

**Q.2** After 24 hours, only 0.125 g out of an initial quantity of 1 g of a radioisotope remains behind. Its half-life period is

- (A) 7.2 h (B) 7.99 h (C) 6.99 h (D) 10.0 h

**Ans.** (B)

**Sol.** In this problem, 'a' = 1.0 g and 'a - x' = 0.125 g and 't' = 24 h. Therefore, the disintegration constant,

$$\lambda = \frac{2.303}{t} \log \frac{a}{a-x}$$

$$\text{Or } \lambda = \frac{2.303}{24} \log \frac{1}{0.125} = 0.0866 \text{ h}^{-1} \quad \text{Or } t_{1/2} = \frac{0.693}{0.0866} = 7.99 \text{ hours}$$

**Q.3** The half-life period of  $\text{I}_{53}^{125}$  is 60 days. What percent of the original radioactivity will be present after 180 days?

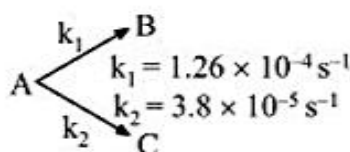
- (A) 50% (B) 20.5% (C) 12.5% (D) 25%

**Ans.** (C)

**Sol.**  $t_{1/2} = 60$  days and  $t = 180$  days

$$\text{Therefore, } t/t_{1/2} = \frac{180}{60} = 3.0 \quad \text{Or } N = \frac{N_0}{2^{3.0}} = \frac{1}{8} N_0 = \frac{1}{8} \times 100 \text{ percent of } N_0 = 12.5\%$$

**Q.4** A radioisotope undergoes decomposition which follows two parallel paths as shown below



The percentage distribution of 'B' and 'C' are

- (A) 80% of 'B' and 20% of 'C' (B) 76.83% 'B' and 23.17% 'C'  
 (C) 90% 'B' and 10% 'C' (D) 60% 'B' and 40% 'C'

**Ans.** (B)



**Sol.** The percent distribution of

$$'B' \text{ is } \frac{k_1}{k_1 + k_2} \times 100 = 76.83 \%, \quad 'C' \text{ is } \frac{k_2}{k_1 + k_2} \times 100 = 23.17\%$$

**Q.5** The activity of 1 g of radium is 0.5 curie. Calculate the half-life period of radium and the time required for the decay of radium from 2.0 g to 0.25 g.

(Atomic mass = 226)

**Ans.** 9492 yrs.

**Sol.** Number of atoms in 1.0 g of  $^{226}\text{Ra} = \frac{6.023 \times 10^{23} \times 1.0}{226}$

$$\text{Activity } -\frac{dN}{dt} = 0.5 \text{ curie}$$

$$= 0.5 \times 3.7 \times 10^{10} \text{ disintegrations per second}$$

$$= 1.85 \times 10^{10} \text{ disintegrations per second}$$

$$-\frac{dN}{dt} = \lambda N \quad \text{or } 1.85 \times 10^{10} = \lambda \times \frac{6.023 \times 10^{23}}{226}$$

$$\text{Or } \lambda = 6.945 \times 10^{-12} \text{ s}^{-1} \quad \text{Or } t_{1/2} = \frac{0.693}{6.945 \times 10^{-12}} = 9.978 \times 10^{10} \text{ s}$$

$$= \frac{9.978 \times 10^{10}}{3600 \times 24 \times 365} \text{ years} = 3164 \text{ years}$$

Time required for the decay of 2.0 g to 0.25 g = three half lives =  
 $3 \times 3164 = 9492 \text{ years}$

**Q.6** A certain radioisotope  $^A_Z\text{X}$  ( $t_{1/2} = 10$  days) decays to give  $^{A-4}_{Z-2}\text{Y}$ . If 1.0 g atom of  $^A_Z\text{X}$  is kept in a sealed vessel, how much helium will collect in 20 days?

**Ans.** 16.8 L

**Sol.** Decay of  $^A_Z\text{X}$  to  $^{A-4}_{Z-2}\text{Y}$  produces one helium atom. Therefore, decay of 1.0 g atom of  $^A_Z\text{X}$  will produce 1.0 g of atom of helium gas. Half-life of X = 10 days.

$$\text{Therefore, the amount decayed in 20 days} = \frac{1}{2} + \frac{1}{4} = \frac{3}{4} \text{ g of atom}$$

$$1.0 \text{ g atom of He} = 22,400 \text{ cm}^3 \text{ at } 0^\circ\text{C and atm}$$

$$3/4 \text{ g atom of He} = 22,400 \times \frac{3}{4} = 16,800 \text{ cm}^3$$

**Q.7** A sample of  $^{14}\text{CO}_2$  was to be mixed with ordinary  $\text{CO}_2$  for a biological tracer experiment. In order that  $10\text{ cm}^3$  of diluted gas should have  $10^4$  dis/min, what activity (in  $\mu\text{Ci}$ ) of radioactive carbon is needed to prepare 60 L of diluted gas at STP. [1 Ci =  $3.7 \times 10^{10}$  dps]

- (A)  $270\ \mu\text{Ci}$  (B)  $27\ \mu\text{Ci}$  (C)  $2.7\ \mu\text{Ci}$  (D)  $2700\ \mu\text{Ci}$

**Ans.** (B)

**Sol.**  $A = \lambda N$ ; activity (or rate of decay) of 10 ml gas  $\Rightarrow \frac{10^4}{60}$  dps

$$\text{rate of decay of 60 litre gas} = \left(\frac{10^4}{60}\right) \times \frac{60 \times 1000}{10} = 10^6 \text{ sec}$$

$$(\because 1 \text{ Ci} = 3.7 \times 10^{10} \text{ dps}) \quad = \frac{10^6}{3.7 \times 10^{10}} = 27 \times 10^{-6} \text{ Ci} = 27\ \mu\text{Ci} \text{ Ans.}$$

**Q.8** The analysis of a mineral of uranium reveals that ratio of mole of  $^{206}\text{Pb}$  and  $^{238}\text{U}$  in sample is 0.2. If effective decay constant of process  $^{238}\text{U} \longrightarrow ^{206}\text{Pb}$  is  $\lambda$  then age of rock is

- (A)  $\frac{1}{\lambda} \ln \frac{5}{4}$  (B)  $\frac{1}{\lambda} \ln \left(\frac{5}{1}\right)$  (C)  $\frac{1}{\lambda} \ln \frac{4}{1}$  (D)  $\frac{1}{\lambda} \ln \left(\frac{6}{5}\right)$

**Ans.** (D)

**Sol.**  $t = \frac{1}{\lambda} \ln \left[ \frac{n_{\text{Pb}} + n_{\text{U}}}{n_{\text{U}}} \right] \quad \dots(i)$

given  $\frac{n_{\text{Pb}}}{n_{\text{U}}} = 0.2 = \frac{1}{5} \Rightarrow \left( \frac{n_{\text{Pb}} + n_{\text{U}}}{n_{\text{U}}} \right) = \frac{1}{5} + 1 = \left( \frac{6}{5} \right) \quad \dots(ii)$

Substituting (ii) in (i)

$$t = \frac{1}{\lambda} \ln \left( \frac{6}{5} \right)$$

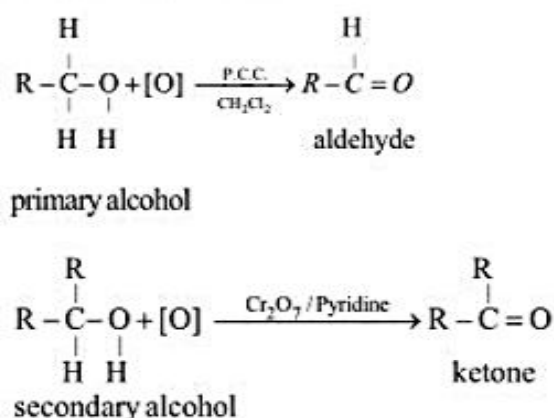
## CARBONYL COMPOUND

### INTRODUCTION

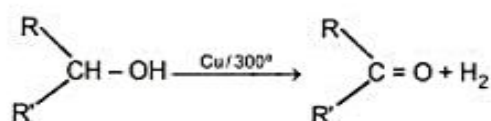
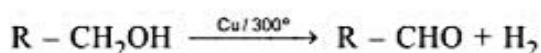
- (a) Organic compounds in which  $\begin{array}{c} \text{O} \\ \parallel \\ \text{C} \end{array}$  group is present are called 'Aldehyde & Ketone'.
- (b) The group  $\begin{array}{c} \text{O} \\ \parallel \\ \text{C} \end{array}$  is called as carbonyl group so, compound are also called carbonyl compounds. If H atom is attached with this carbonyl group then compound is called **aldehyde** and if alkyl group is present on both sides then compound is called **Ketone**.
- (c) In ketone if both alkyl group are same then they are called simple ketone, if different then called mixed ketone.
- (d) Their general formula is  $\text{C}_n\text{H}_{2n}\text{O}$ . Hybridisation state of carbon is  $\text{sp}^2$  and  $\text{C}=\text{O}$  bond length is  $1.23 \text{ \AA}$ .
- (e) The ratio of C, H & O in formaldehyde is  $1 : 2 : 1$  ( $\text{CH}_2\text{O}$ ). It is called simplest sugar.
- (f) Aldehyde shows chain, position and functional isomerism.
- (g) Ketone shows chain, position, functional and metamerism also. Aldehyde and ketone both are functional isomers with each other.

### GENERAL METHODS OF PREPARATION

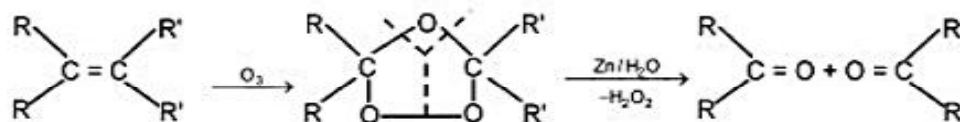
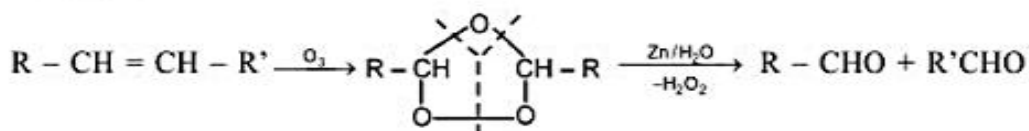
**From Alcohol (By Oxidation) :-** Primary alcohols can be oxidised to aldehydes by using pyridinium chlorochromate (P.C.C) ( $\text{C}_5\text{H}_5\text{NH}^+\text{CrO}_3\text{Cl}^-$ ). A stronger oxidising agent (e.g.  $\text{KMnO}_4$ ) oxidises primary alcohols to carboxylic acids.



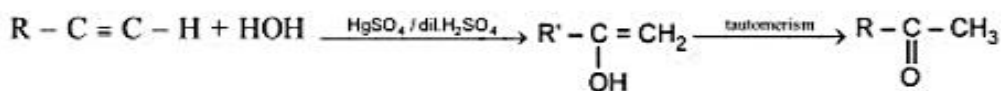
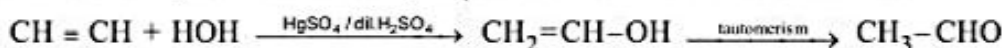
**From Alcohol (By Catalytic Oxidation) :-** When vapours of a primary alcohol (or secondary alkanol) are passed over heated copper (or zinc oxide) at  $300^\circ$  then aldehyde (or ketones) are formed.



**From Alkene (Ozonolysis) :** Desired aldehyde and ketones can be obtained by ozonolysis of appropriate alkenes.

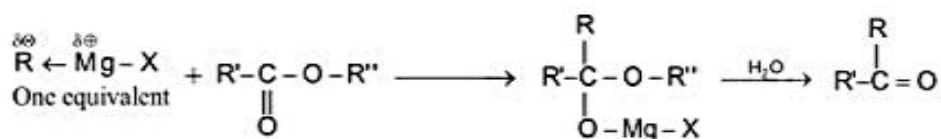


**From Alkyne :** Acetaldehyde is formed on passing acetylene in 40% aqueous solution of  $H_2SO_4$  at  $60^\circ$  in the presence of 1%  $HgSO_4$ . It is called **Kucherov's reaction**.

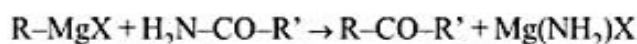
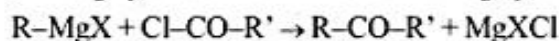
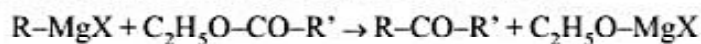


**Note :** Methanal cannot be formed from the above reaction.

**From Grignard's Reagent :** Alkanal is formed by reaction of formic ester and an alkylmagnesium halide.



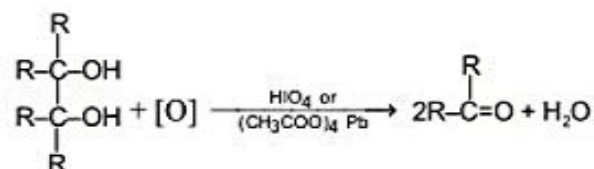
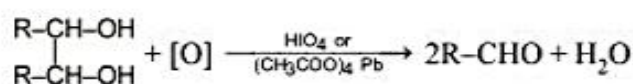
Ketones are obtained from acetic and higher esters. Acid chlorides and amides can be taken in place of esters. However  $HCOCl$  cannot be taken because it is unstable.



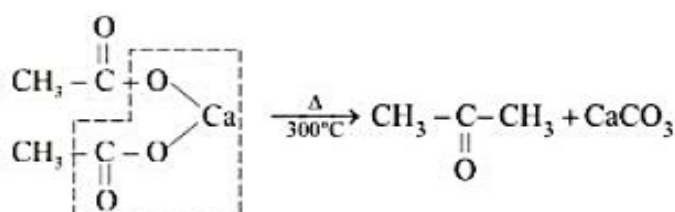
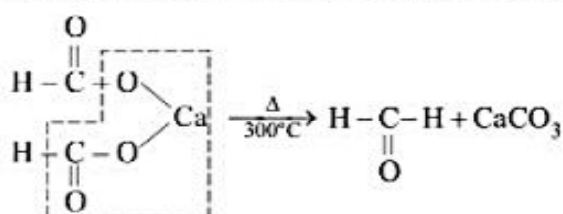
**Note :** Formaldehyde cannot be formed from the above reaction.

**From Vicinal Glycol (Oxidation) :** Carbonyl compounds are obtained on oxidation of vicinal alkanediols by periodic acid or lead tetraacetate

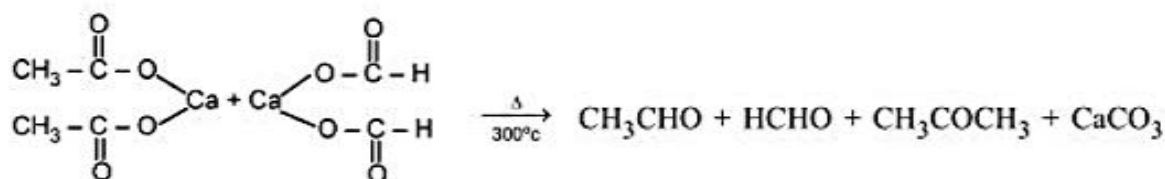




**From Calcium or Barium salt of Carboxylic acid :** When calcium salts of alkanolic acids are subjected to dry distillation, then carbonyl compounds are formed. The yield increases on taking barium, manganese and thorium salts of alkanolic acids. Formaldehyde is formed on taking calcium formate ( $\text{R} = \text{H}$ ) and acetone is formed on taking calcium acetate ( $\text{R} = \text{CH}_3$ ).

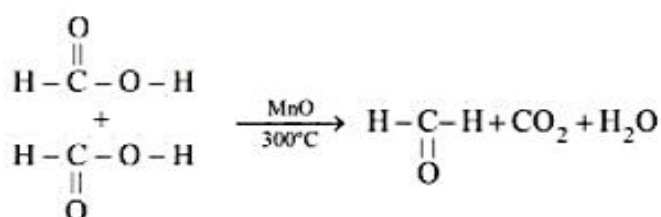


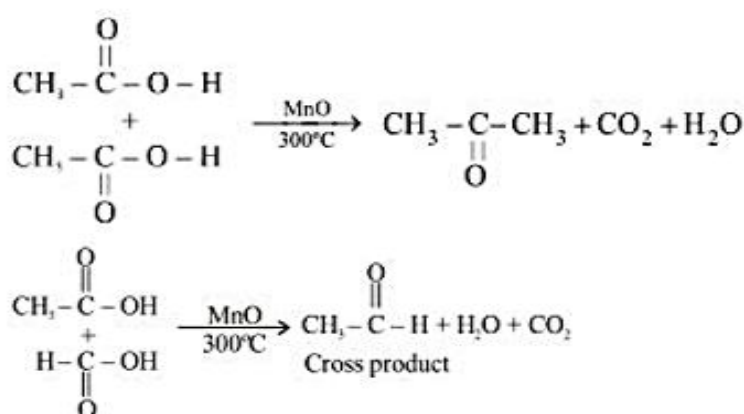
Acetaldehyde can be formed by taking a mixture of calcium formate and calcium acetate.



**From Carboxylic Acid : –** When vapours of carboxylic acid are passed on manganese oxide  $\text{MnO}$  at  $300^\circ\text{C}$ , then carbonyl compounds are formed.

Formaldehyde is prepared from formic acid ( $\text{R} = \text{R}' = \text{H}$ ), acetone from ( $\text{R} = \text{R}' = \text{CH}_3$ ), and acetaldehyde from a mixture of acetic acid ( $\text{R}' = \text{CH}_3$ ) and formic acid ( $\text{R} = \text{H}$ ).

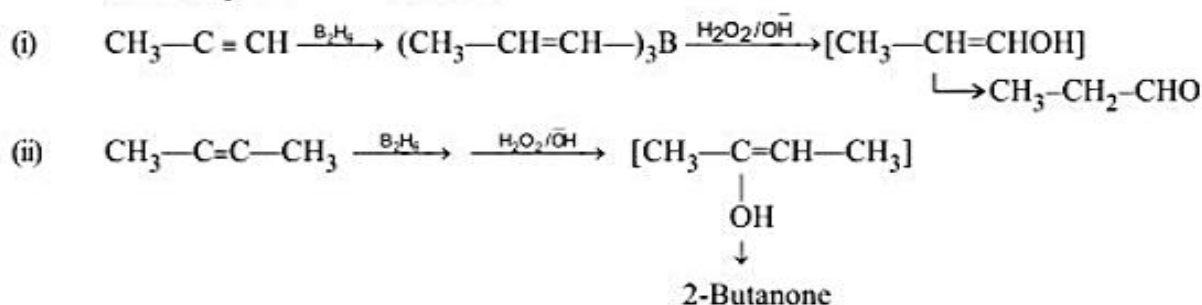




**From Alkyne (Hydroboration) :** When a dialkylborane is reacted with an alkyne, then dialkylvinylborane adduct is formed, which on reacting alkaline hydrogen peroxide solution forms a carbonyl compound. Alkanals are formed from terminal alkynes, and alkanones from nonterminal alkynes.

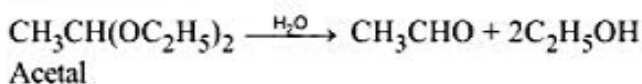
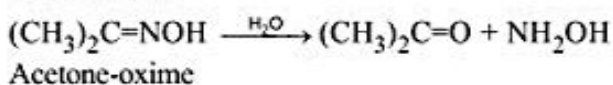
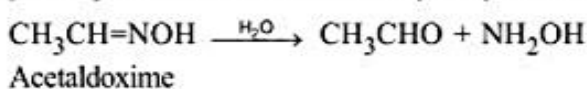
1-Alkyne  $\longrightarrow$  Aldehyde

Other alkynes  $\longrightarrow$  Ketone



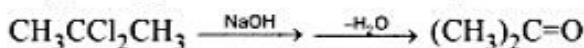
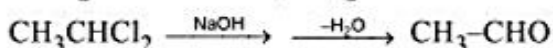
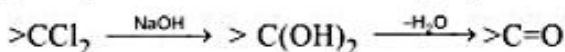
#### By the Hydrolysis of oximes and acetals :

Carbonyl compounds are formed from hydrolysis of oximes and acetals.



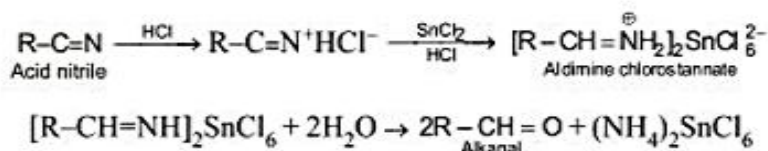
#### By the Hydrolysis of gemdihalide :

Carbonyl compounds are formed on heating alkylidene dihalides with aqueous caustic alkali solution.

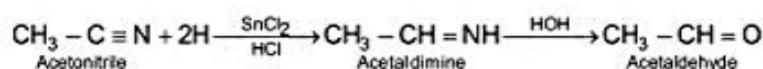


## METHODS OF PREPARATION ONLY FOR ALDEHYDES

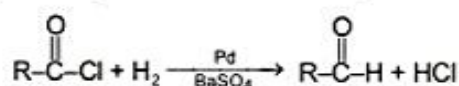
**Stephen's Method :** By dissolving an alkyl cyanide in ether and reacting it with stannous chloride and conc. hydrochloride, aldimine chlorostannate salt is obtained. Alkanal is formed on hydrolysis of this salt.



Taking the example of acetonitrile (methyl cyanide) Stephen reaction can be shown expressed as follows.

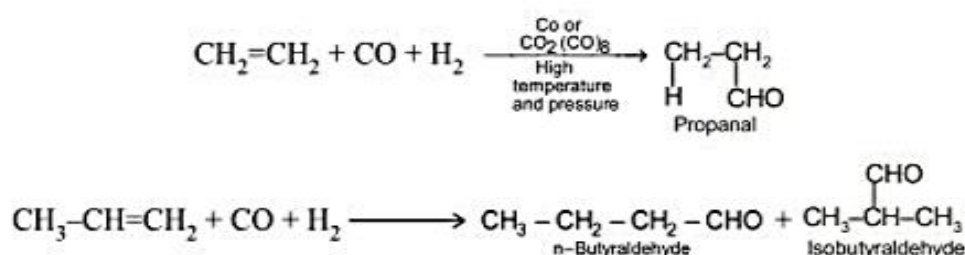


**Rosenmund Reaction :** Aldehydes are formed on reduction of a carboxylic acid chloride in boiling xylene medium by hydrogen and palladised barium sulphate.



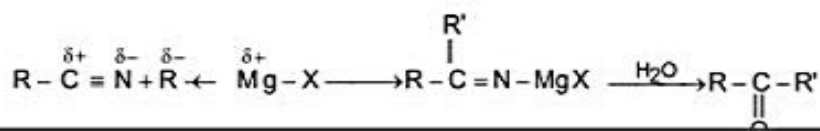
Acetaldehyde is formed on taking acetyl chloride ( $\text{R} = \text{CH}_3$ ). Formaldehyde cannot be prepared by Rosenmund reaction, because  $\text{HCOCl}$  is not a stable compound,  $\text{BaSO}_4$  acts as a catalyst poison and decreases the catalytic efficiency of  $\text{Pd}$  catalyst, due to which further reduction of acetaldehyde formed to primary alcohol cannot take place.

**Oxo-reaction :** When a mixture of an alkene, carbon monoxide and hydrogen is passed over cobalt catalyst at high temperature and pressure, then alkanals are formed. Dicobalt octacarbonyl  $[\text{Co}_2(\text{CO})_8]$  can be used as a catalyst in place of cobalt. Due to addition of hydrogen and formyl group on unsaturated carbon atoms of alkene, this reaction is called hydroformylation.



## METHODS OF PREPARATION ONLY FOR KETONES

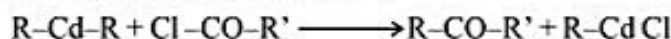
**From Alkyl Cyanide :** Alkanones are formed on hydrolysis after reaction of an alkylmagnesium halide with ethyl cyanide or its higher homologue.





In this reaction if we take HCN with GR., product will be aldehyde but major product will be alkane because HCN is an example of active H compound and with active hydrogen compound GR forms alkane.

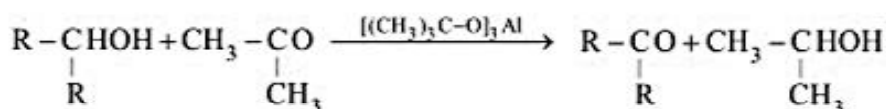
**Dialkyl cadmium with acid chlorides :** A ketone and an alkylcadmium chloride are formed on reacting a dialkylcadmium with an acid chloride.



Dialkylcadmium are obtained by the reaction of cadmium chloride with a Grignard's reagent.



**Oppenaur Oxidation :** In order to prepare alkanone easily, Oppenauer oxidation of secondary alkanols is done. In this process, a secondary alkanols is refluxed with aluminum tert-butoxide in excess amount in acetone. Acetone is reduced to isopropyl alcohol.

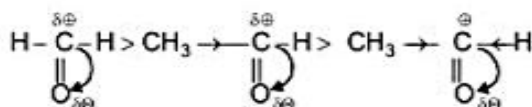


## PHYSICAL PROPERTIES

- (a) Aldehydes are colourless with pungent smell liquid while ketones are pleasant smell liquids but formaldehyde is gaseous in nature.
- (b) Lower carbonyl compounds are soluble in water. It is due to polarity in carbonyl group.
- (c) Higher carbonyl compounds are insoluble in water due to more covalent character.
- (d) Melting point & Boiling point  $\propto$  Molecular mass

$$\propto \frac{1}{\text{No. of branches}}$$

- (e) Melting point and boiling point of carbonyl compounds are more than to corresponding alkanes due to dipole-dipole attraction present between molecules in carbonyl compounds.
- (f) Reactivity of carbonyl compound is dependent on alkyl group which is linked with carbonyl group.



- (g) 40% solution of formaldehyde is known as '**FORMALIN**' (40% HCHO, 54-56% H<sub>2</sub>O, 4-6% methanol)
- (h) Mixture of formaldehyde and lactose sugar is called '**FORMAMINT**' which is used in medicine of throat infection.
- (i) Boiling point of carbonyl compounds are as under -

S.No.	Compound	Boiling Point
1.	Formaldehyde	- 21°C
2.	Acetaldehyde	+ 21°C
3.	Acetone	56°C

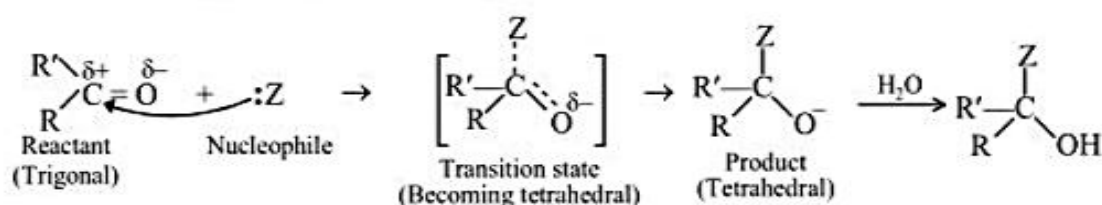


## CHEMICAL PROPERTIES

### Nucleophilic Addition Reactions

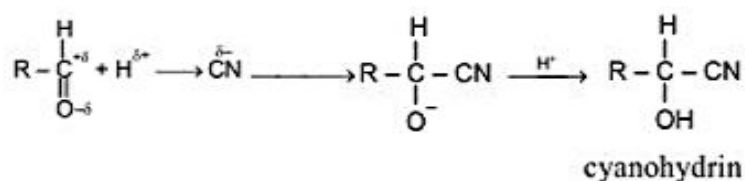
The typical reactions of aldehydes and ketones are nucleophilic addition reactions because

- the carbonyl carbon is electron deficient, since  $\pi$ -electrons are pulled towards the electronegative oxygen, and
- this part of molecule being flat is open to relatively unhindered attack



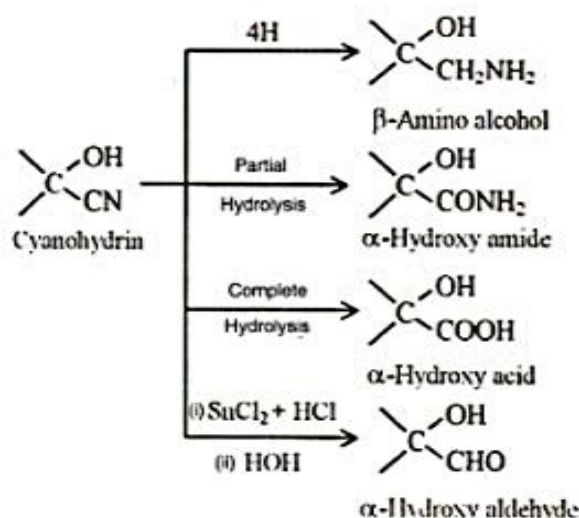
**Note :** There is a moderate steric hindrance in the transition state, that is, larger groups (R & R') will tend to resist crowding than smaller groups. Aldehydes thus undergo nucleophilic addition reactions faster than ketones. Thus, among the compounds  $\text{HCHO}$ ,  $\text{CH}_3\text{COCH}_3$ , and  $\text{CH}_3\text{CHO}$ , the order of reactivity to nucleophilic addition will be  $\text{HCHO} > \text{CH}_3\text{CHO} > \text{CH}_3\text{COCH}_3$ .

### Reaction with Hydrogen Cyanide : -



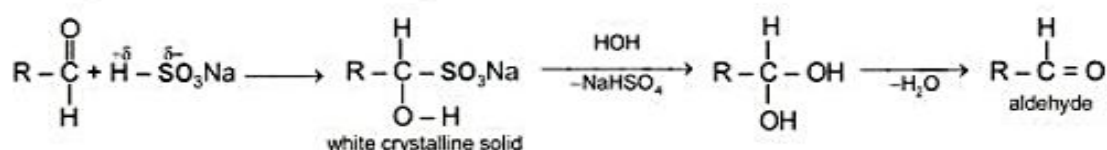
### Note : -

- Reaction takes place in presence of mild base which abstract  $\text{H}^+$  from  $\text{HCN}$  and produce  $\text{CN}^-$  ion which acts as nucleophile.
- If  $\text{R} = \text{H}$  then product will be formaldehyde cyanohydrin.
- Cyanohydrin is an important compound which gives the following product on hydrolysis and reduction.



**Reaction with Sodium bisulphite :**

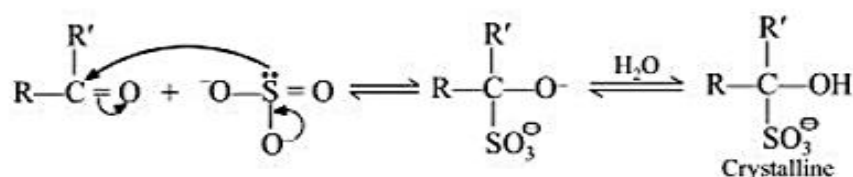
Carbonyl compound form a white crystalline addition product with sodium bisulphite called **Aldehyde / Ketone sodium bisulphite adduct**.



**Mechanism :** The attacking nucleophile is  $\text{SO}_3^{2-}$  rather than  $\text{HSO}_3^-$ .

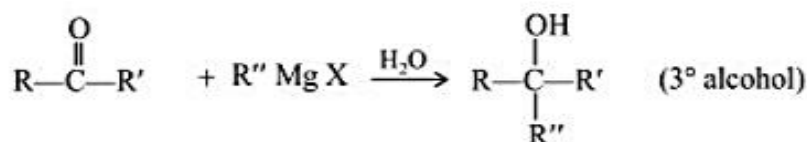
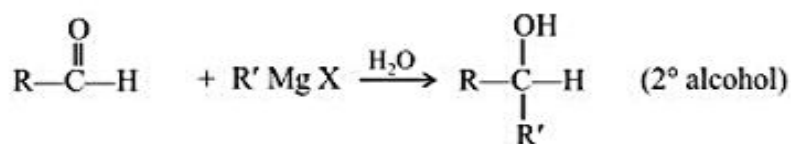
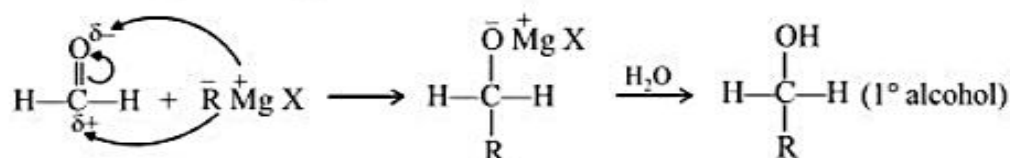


Though  $\text{HSO}_3^-$  is present in higher concentration,  $\text{SO}_3^{2-}$  is a better nucleophile.



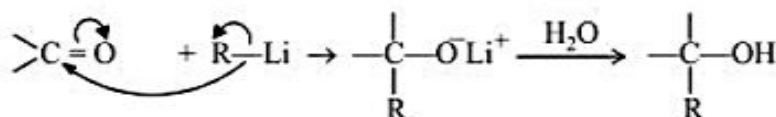
**Note : -**

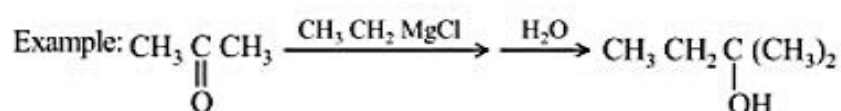
- Bisulphite adduct is an important compound because it gives carbonyl compound on further hydrolysis.
- The above reaction is used in purification of carbonyl compound.
- The reaction is given by only methyl ketone & aldehyde.

**Reaction with Grignard Reagents**

Formaldehyde yields primary alcohols, higher aldehydes produce secondary alcohols, and ketones produce tertiary alcohols with Grignard reagents.

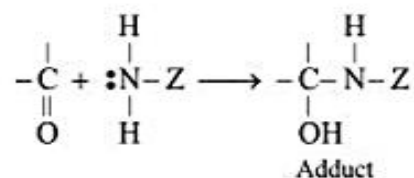
Organolithium compounds also react with aldehydes and ketones in the same manner.



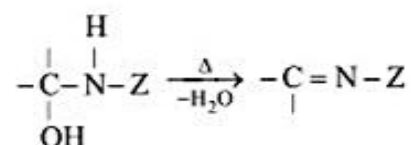


### Reaction with Ammonia derivatives :

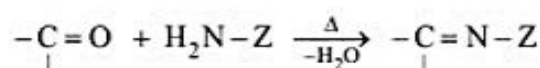
Addition of nitrogenous nucleophile on carbonyl group takes place according to the following mechanism.



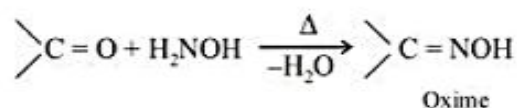
The end product is formed by elimination of water from the adduct under appropriate energy condition.



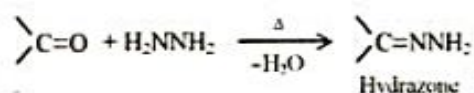
In the above two steps, it appears that an unsaturated condensation product is formed by liberation of the water molecule from carbonyl group and nitrogenous nucleophile.



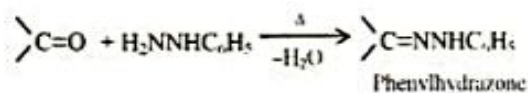
#### (i) With Hydroxylamine :



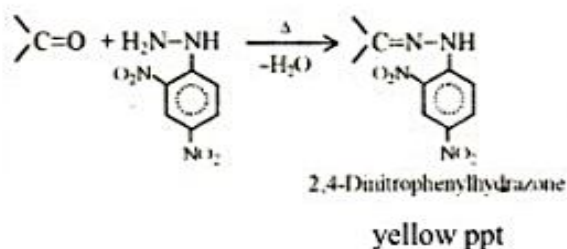
#### (ii) With Hydrazine :



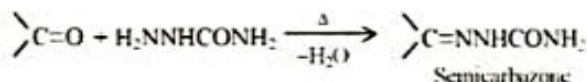
#### (iii) With Phenylhydrazine :



#### (iv) With 2,4-Dinitrophenylhydrazine :



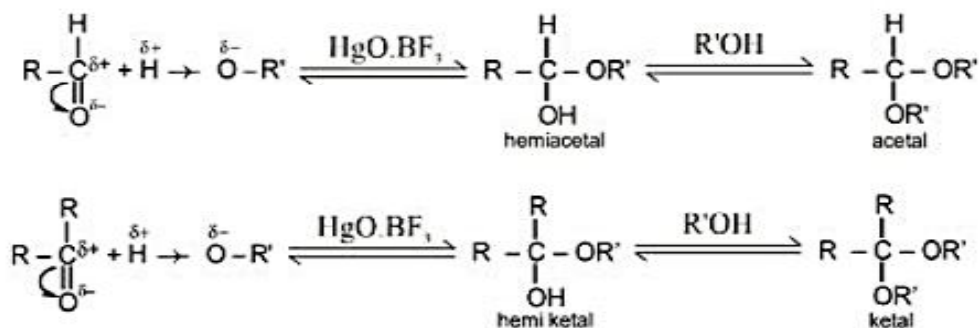
## (v) With Semicarbazide :



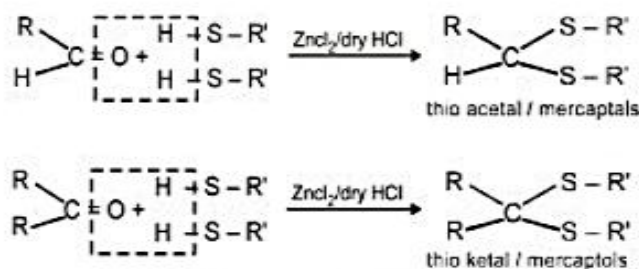
On reacting a carbonyl compound with 2,4-dinitrophenylhydrazine, a yellow precipitate of 2,4-dinitrophenylhydrazone derivative is obtained. White precipitate is obtained by the reaction with hydroxylamine, hydrazine phenylhydrazine and semicarbazide. The pure parent carbonyl compound can be obtained by hydrolysis of the above five derivatives.



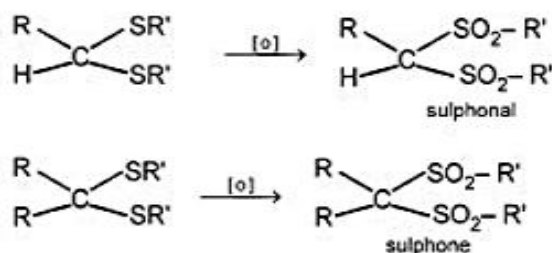
**Reaction with Alcohol :** In the presence of catalyst ( $\text{HgO} \cdot \text{BF}_3$ ) aldehyde form acetal with alcohol while ketone form ketal with alcohol.



**Reaction with Alkane Thiol :** Aldehyde form thio acetal with alkane thiol while ketone form thio ketal with alkane thiol.



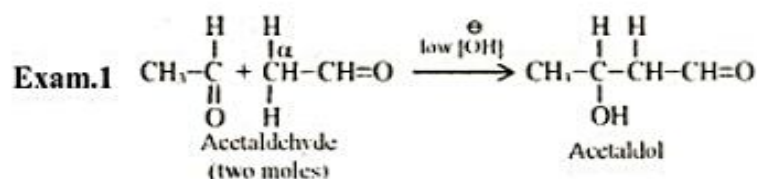
These are important compounds because they form sulphonyl compounds on oxidation which are used as hypnotic drugs.



**Aldol Condensation :** In the presence of small amounts of hydroxide ions (base) two molecules of the carbonyl compound containing  $\alpha$ -hydrogen atoms, give a  $\beta$ -hydroxy carbonyl compound. This reaction is normally called Aldol condensation. Aldol condensation of two identical carbonyl compounds is called simple aldol condensation.

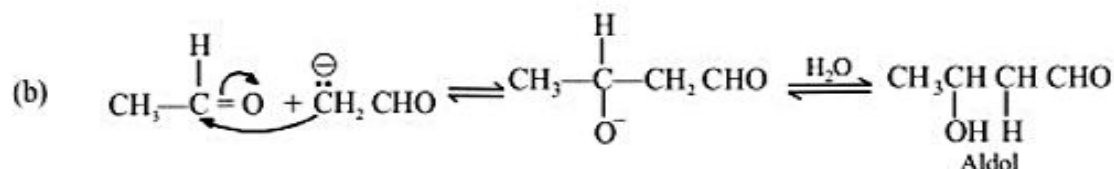
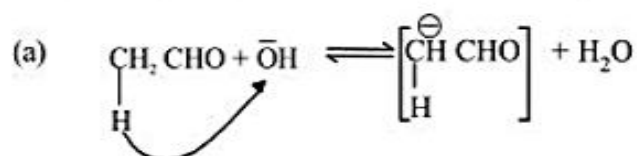


As a source of hydroxide ions, a few drops of very dilute aqueous solution of  $K_2CO_3$ ,  $Na_2CO_3$ ,  $NaOH$ ,  $KOH$ ,  $Ca(OH)_2$ ,  $Ba(OH)_2$  etc. are added.



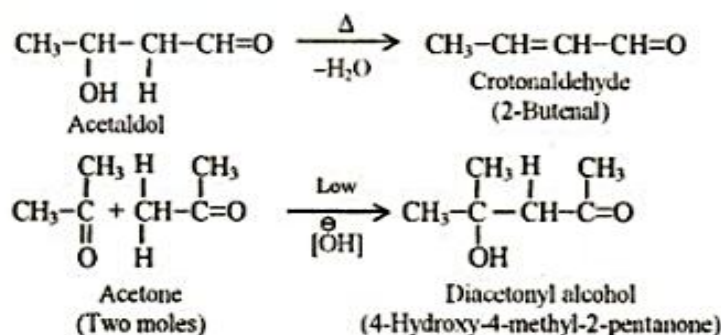
### Mechanism :

The generally accepted mechanism for base-catalysed condensation involves the following steps:

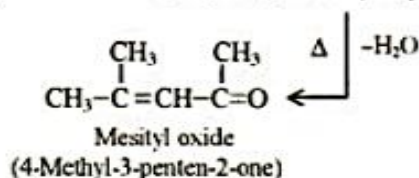


$\beta$ -hydroxy aldehydes or ketones obtained are easily dehydrated, yielding a stable alkene in which a carbon-carbon double bond is conjugated with a carbon-oxygen double bond of the carbonyl group.

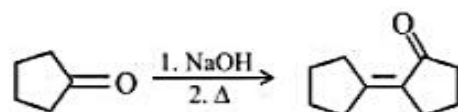
A  $\alpha$ ,  $\beta$ -unsaturated aldehyde crotonaldehyde is formed by the elimination of a water molecule on heating  $\beta$ -hydroxy butanol (3-hydroxybutanal)

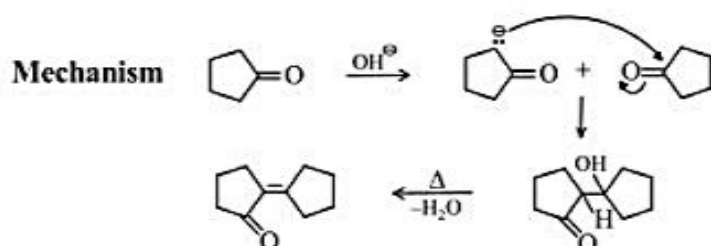


### Exam. 2

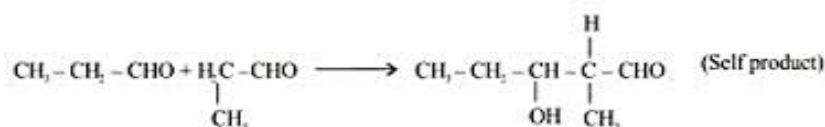
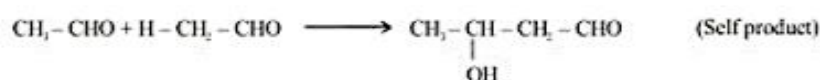
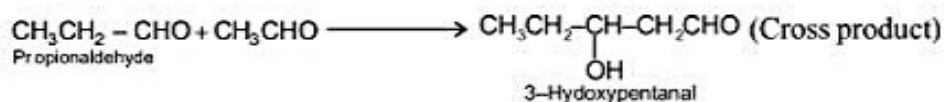
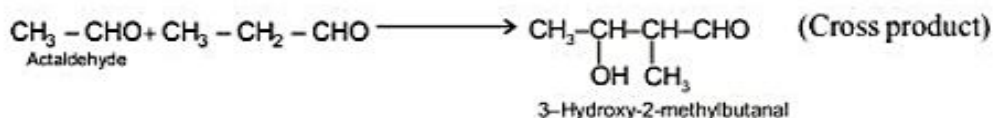


### Exam.3



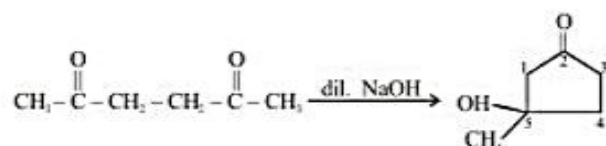


Aldol condensation of two non identical carbonyl compounds is called mixed or **cross aldol condensation**. Theoretically four products can be formed from aldol condensation of the carbonyl compounds A and B.

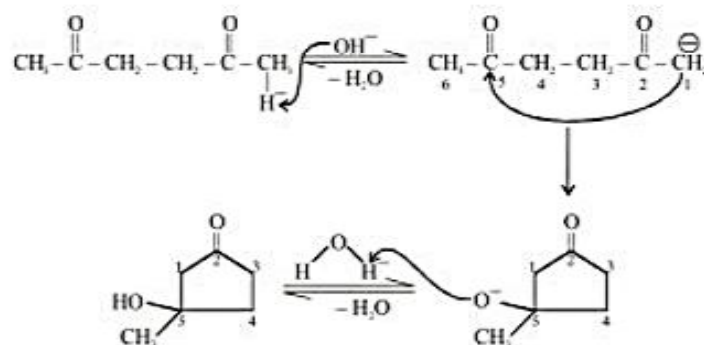


**Intramolecular aldol condensation :** It is given by dialdehydes or diketones. The diketones should be 2, 5; 2, 6; 2, 7; and 2, 8 diketones. Intramolecular aldol condensation offers a convenient method for the preparation of five & six membered rings. 2, 7 diketones gives five membered cyclic compound whereas 2, 8-diketones gives six membered cyclic compound.

**Ex.**



**Mechanism-**

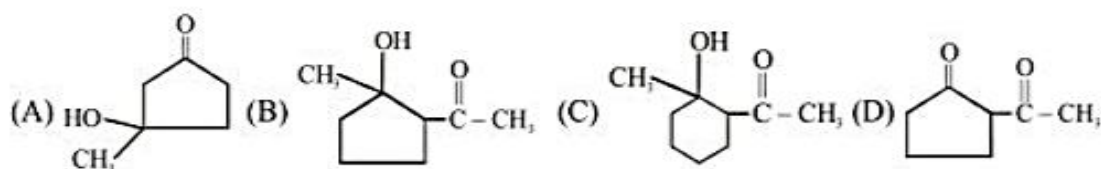


**Note :-** If diketones is 2, 7; 2, 8 or 2, 9 then inner  $\alpha$ -carbon converts into carbanion in the presence of base.

Ex.

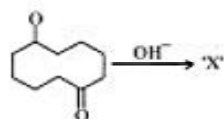


Product 'X' is

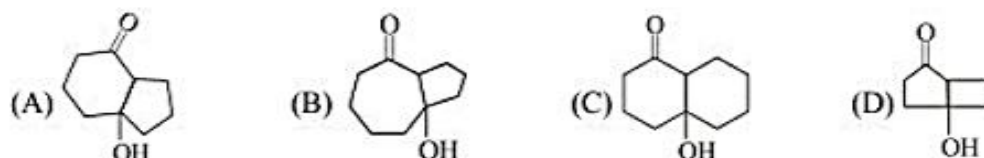


Ans. B

Ex.



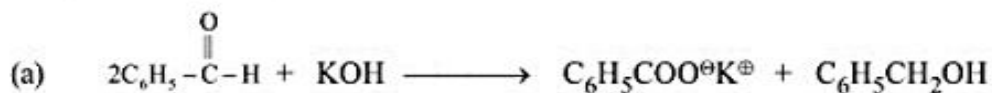
X is-



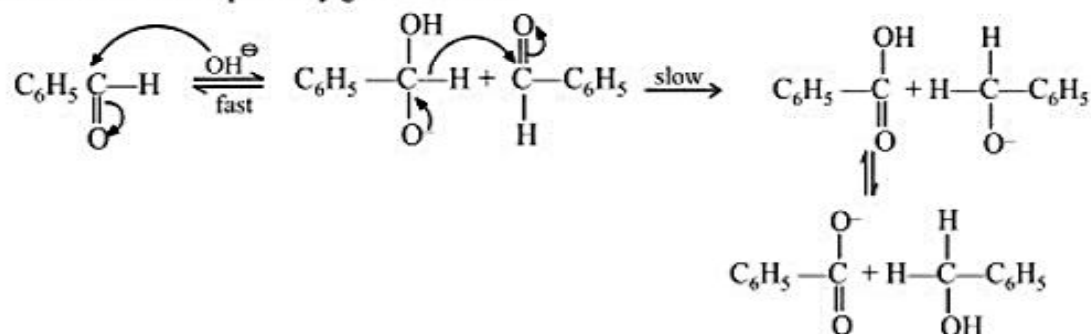
Ans. (B)

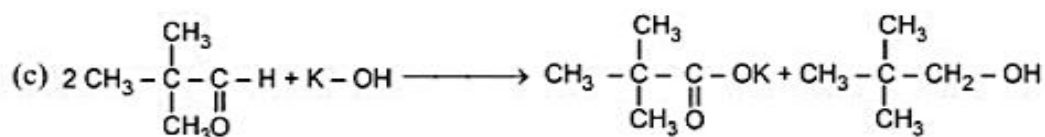
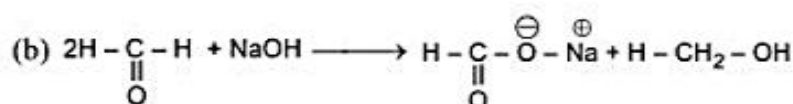
**Cannizzaro Reaction :** Carbonyl compound in which  $\alpha$ -H atom is absent, when react with strong base like NaOH or KOH then forms sodium and potassium salt of carboxylic acid and alcohol. It is an example of the reaction in which one mole of the compounds is reduced. Such type of reaction is called disproportionation reaction, also known as cannizzaro reaction. In this reaction elimination of hydride ion takes place. In this reaction oxidation number changes from 0 to +2 and 0 to -2.

Compounds showing cannizzaro reaction are -



The reaction follows the pathway given below :





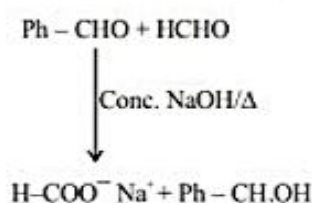
**Note : -**

(i)  $\text{CH}_3-\text{CH}-\text{CHO}$  gives cannizaro reaction although it has one  $\alpha$  'H'.

(ii)  $\text{CCl}_3-\text{CHO}$  does not give cannizaro reaction while it has no ' $\alpha$ ' H. It gives haloform reaction

(iii) Cannizaro reaction is an example of disproportionation reaction and it is also an example of redox reaction

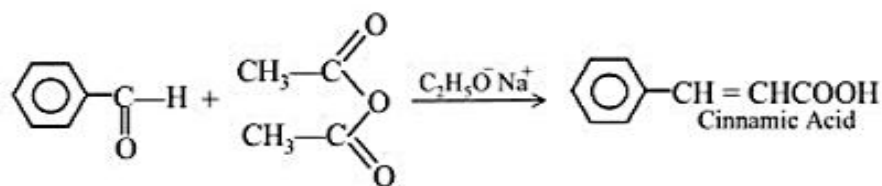
**Cross Cannizaro Reaction :** If two different aldehydes ( $\alpha$ -hydrogen less) are used then one of the aldehyde under goes oxidation while other aldehyde under goes reduction



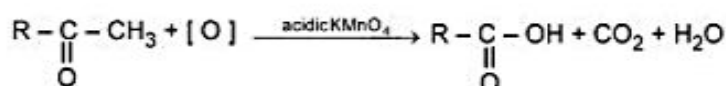
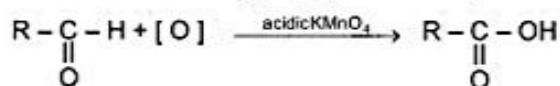
**Note :**  $\alpha$ -hydrogen less aldehyde having more electron deficient carbonyl carbon under goes oxidation.

### Perkin Condensation

Aromatic aldehydes lacking  $\alpha$ -hydrogen condense with acid anhydrides having an  $\alpha$ -hydrogen in the presence of a strong base (ethoxide ion), forming unsaturated acids.



**Oxidation :** Aldehyde on oxidation forms respective acid while ketone forms less carbon carboxylic acid on oxidation according to popoff's rule (As discussed in Alcohol theory)

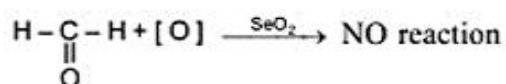


**Note :-**

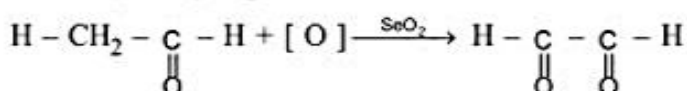
(a) If oxidising agent is selenium oxide  $\text{SeO}_2$  then,  $\alpha$ -methylene group of carbonyl compound oxidises into  $-\overset{\text{O}}{\parallel}{\text{C}}-$  group and resultant dicarbonyl compound will be formed.

$\text{O}$



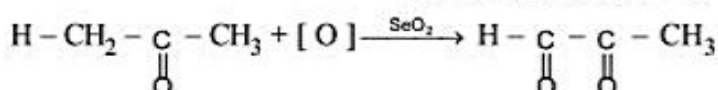


$\alpha$  - methylene group is absent.



glyoxal

(dicarbonyl compound)

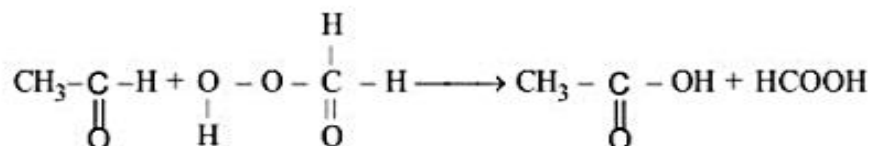
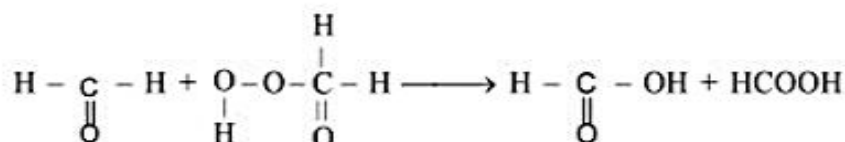


pyruvic aldehyde

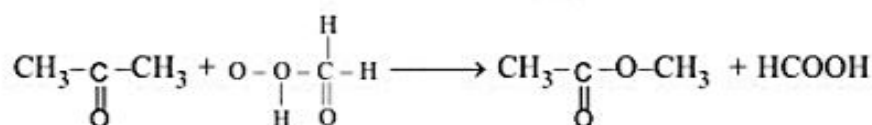
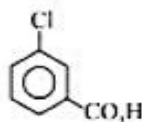
(methyl glyoxal)

- (b) If the oxidising agent is performic acid then aldehyde oxidises into respective acid while ketone oxidises into ester. The reaction is called '**Baeyer-villiger Oxidation**'. Other peroxy acid also give same product.

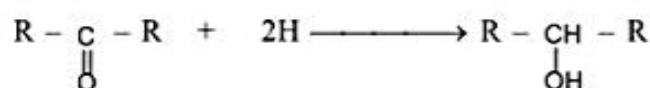
eg.  $\text{CH}_3\text{COOOH}$ ,  $\text{C}_6\text{H}_5\text{COOOH}$ , MCPBA,  $\text{CF}_3\text{COOOH}$



\*\*\* MCPBA  $\rightarrow$  meta chloro perbenzoic acid



**Reduction :** Aldehyde on reduction form primary alcohol while ketone on reduction form secondary alcohol.



secondary alcohol

**Note :**

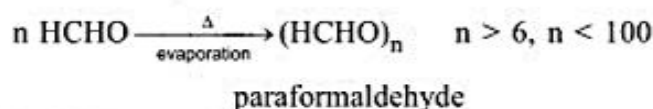
- In the above reaction if reducing agent is  $\text{Na} + \text{C}_2\text{H}_5\text{OH}$  then reaction is called '**Bouveault- Blanc Reaction**'.
- If reducing agent is  $\text{NaH}$  reaction is called '**Darzen's Reaction**'. We can also use  $\text{LiAlH}_4$  in this reaction.
- If reducing agent is (red P / HI) then product will be alkane.
- If reducing agent is  $\text{Zn-Hg}/\text{conc. HCl}$  then product will be alkane. Reaction is called '**Clemmenson-Reduction**'.
- If reducing agent is alkaline solution of hydrazine, product will be alkane. Reaction is called '**Wolf - kishner Reduction**'.
- The percentage yield of alkane can be increased by using diethylene glycol in wolf kishner reduction then reaction is called '**Huang-Millan Conversion**'.
- If reducing agent is aluminium iso propoxide  $(\text{CH}_3 - \underset{\text{CH}_3}{\text{CH}} - \text{O})_3\text{Al}$ , then product will be alcohol.

Reaction is called '**Meerwein-Pondorff Verley Reduction**'.

**Polymerisation Reactions :** Aldehyde shows addition as well as condensation polymerisation reactions while ketone shows only condensation polymerisation reactions.

## ADDITION POLYMERISATION REACTION OF FORMALDEHYDE

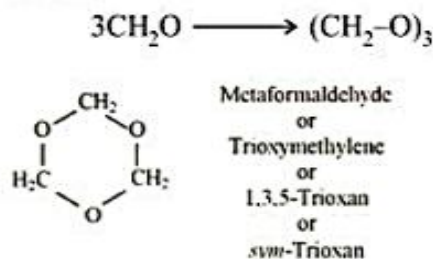
- When aqueous solution of formaldehyde is heated then it converts into a white crystalline solid called '**Paraformaldehyde**'.



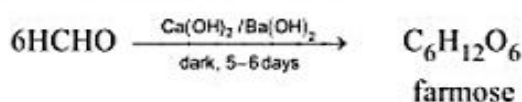
If  $n \leq 50$  Linear structure polymer

If  $n > 50$  Cyclic structure polymer

- If formaldehyde is kept with conc.  $\text{H}_2\text{SO}_4$  at room temperature then it forms a cyclic trimer called meta formaldehyde or trioxane.

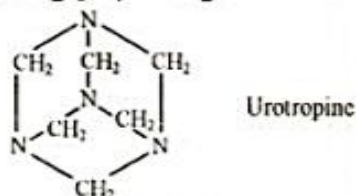
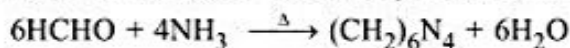


- If aqueous solution of formaldehyde is kept with lime water in dark room for 5-6 days then it converts into a sweet solution called '**FARMOSE**'. It is an example of linear polymer.



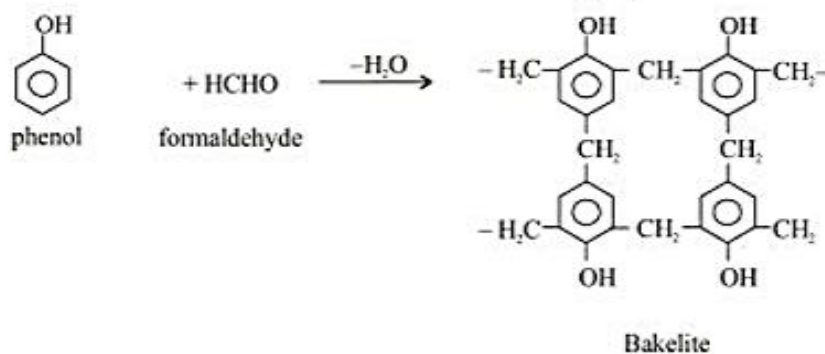
## CONDENSATION POLYMERISATION REACTION OF FORMALDEHYDE

- (a) **With Ammonia** :– When formaldehyde is heated with  $\text{NH}_3$  then a white crystalline heterocyclic compound is formed called 'Hexamethylene tetramine' or urotropene' or 'Aminoform'.



It is used in medicine or diabetes or urinary infection.

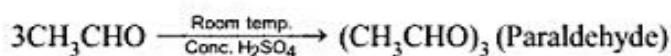
- (b) **With Phenol** :– In presence of dilute alkali formaldehyde first form o- & p- hydroxy benzyl alcohol with phenol which on self condensation form a cross link polymer called 'Bakelite'.



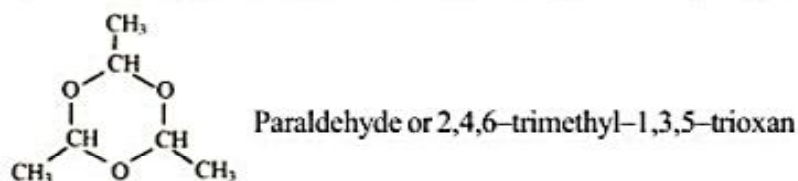
Bakelite is electric and thermal resistant. So, used in formation of electric appliances. Reaction is called 'Lederer-Manasse Reaction'.

### Addition Polymerisation of Acetaldehyde :

- (a) When acetaldehyde is kept with conc.  $\text{H}_2\text{SO}_4$  at room temperature then it form a cyclic trimer called paraldehyde.

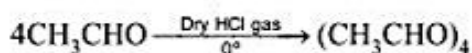


Paraldehyde has nonaromatic heterocyclic structure and it is called 2,4,6-trimethyl-1,3,5-trioxan.

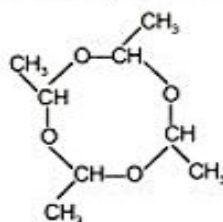


Paraldehyde is used as mild hypnotic.

- (b) If acetaldehyde is kept with highly conc.  $\text{HCl}$  at low temperature then it forms a cyclic tetramer called metaaldehyde.



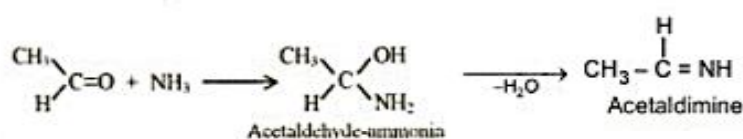
Metaldehyde has the following nonaromatic eight-membered heterocyclic structure.



**Note :** Metaldehyde is used as smokeless powder and Para aldehyde is used as a sedative while meta aldehyde is used as a solid fuel.

#### Condensation Polymerisation of Acetaldehyde : –

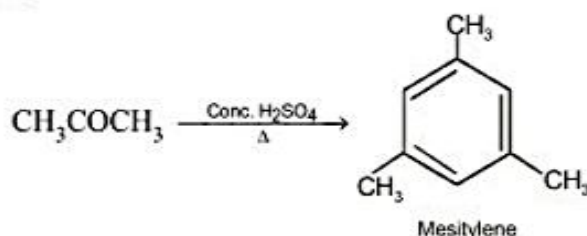
- (a) **Aldol condensation** – Discussed earlier.
- (b) **Reaction with  $\text{NH}_3$  :**



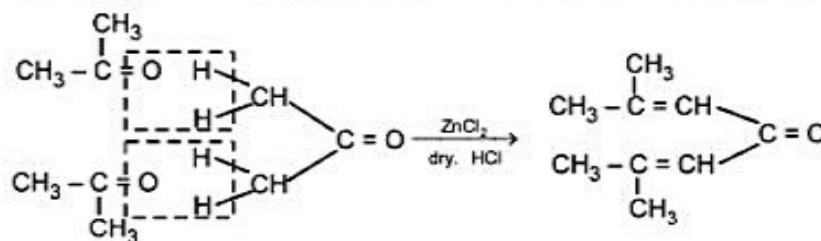
Acetaldimine is formed by the elimination of water molecule on heating acetaldehyde-ammonia, which undergoes polymerisation to form a nonaromatic heterocyclic addition trimer, name 2,4,6-trimethylhexahydro-1,3,5-triazine trihydrate as the main product.

#### Condensation Polymerisation of Acetone :

- (a) If acetone is heated with conc.  $\text{H}_2\text{SO}_4$  then an aromatic compound is formed called 1,3,5-trimethyl benzene or mesitylene.

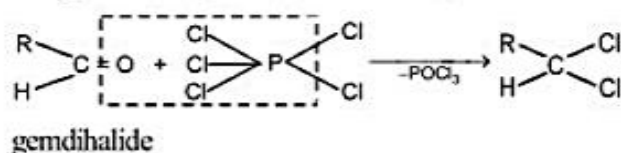


- (b) If acetone would be in excess in ketal condensation or catalyst ( $\text{ZnCl}_2$  / dry  $\text{HCl}$ ) is used then three moles of acetone undergoes condensation polymerisation and form a compound called '**Phorone**'.



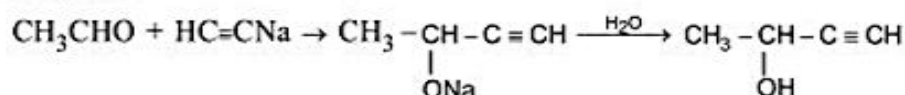
[molecular wt. of phorone = 3 mole of acetone – 2 mole of  $\text{H}_2\text{O}$  ]

**Reaction with  $\text{PCl}_5$  :** Carbonyl compound form gemdihalide with  $\text{PCl}_5$ .

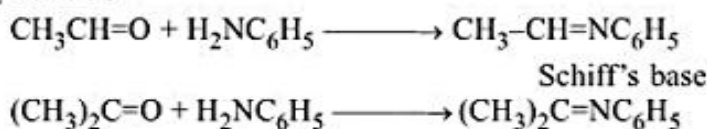




With sodium acetylide :



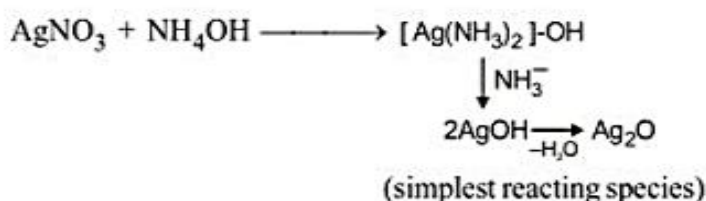
With primary amine :-



## REACTIONS SHOWN BY ALDEHYDES ONLY

**Reducing nature of Aldehyde :** Aldehyde are reducing in nature, they can reduce Tollen's reagent, Fehling solution and mercuric chloride solution.

- (a) **Reaction with Tollen's Reagent :** - Ammonical silver nitrate solution is called Tollen's reagent. Aldehyde reduce the tollen's reagent and form silver mirror. Aldehyde oxidises itself into carboxylic acid.

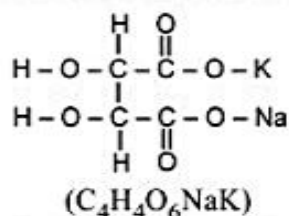


**Note :** In the above reaction oxidation number of Ag varies from +1 to 0.

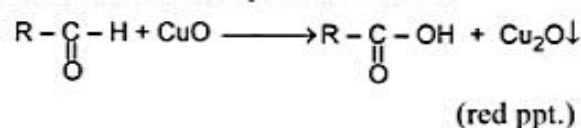
- (b) **Reaction with Fehling Solution :** It is the mixture of two solution called Fehling solution A and Fehling solution B.

**Fehling Solution A :** Aqueous solution of  $\text{CuSO}_4$  (blue)

**Fehling Solution B :** Alkaline solution of Roschelle salt ( sodium potassium tartarate)

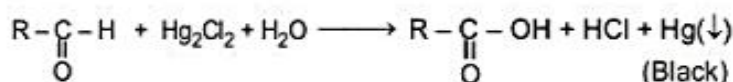


By the mixing of both solution we get a dark blue colour solution called final fehling solution. Reacting species of this solution is cupric oxide  $\text{CuO}$ .



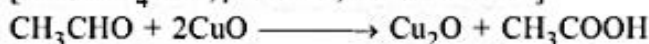
**NOTE :** Oxidation number of copper varies from +2 to +1

- (c) **Reaction with Mercuric Chloride solution :** Aldehyde reacts with mercuric chloride solution and initially form white ppt. of mercurous chloride solution, which further react with excess of aldehyde and form black ppt. of mercury.



- (d) **Benedict solution :**

[A-CuSO<sub>4</sub> soln, β-NaOH, Sodium citrate]

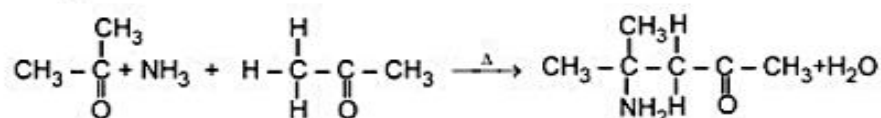


- (e) **Schiff's reagent :**

Magenta dye  $\xrightarrow{\text{SO}_2}$  Colourless solution  $\xrightarrow{\text{CH}_3\text{CHO}}$  Pink colour restored

## REACTIONS SHOWN BY KETONES ONLY

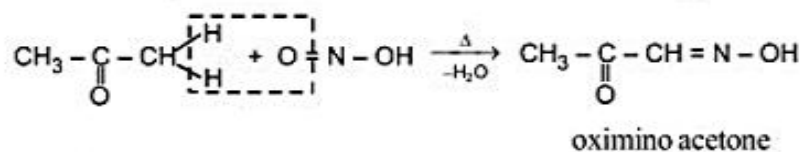
- (a) **Reaction with NH<sub>3</sub> :** If acetone is heated with ammonia then it forms diacetone amine.



If acetone and ammonia would be in excess then product would be tri acetone amine. If tri acetone amine is heated at high temperature then it converts into a heterocyclic compound by the elimination of water.

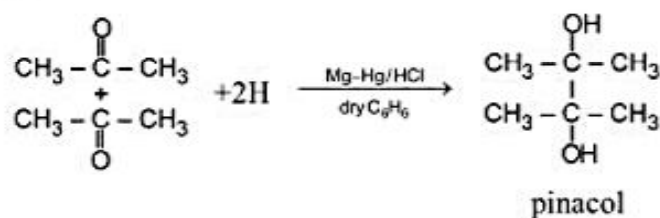
- (b) **Reaction with Nitrous Acid :**

Oximinoacetone is formed by liberation of a water molecule on reacting acetone with nitrous acid.



- (c) **Bimolecular Reduction : -**

Pinacol is formed on reduction of acetone in an inert medium (like benzene) by using magnesium amalgam and hydrogen.

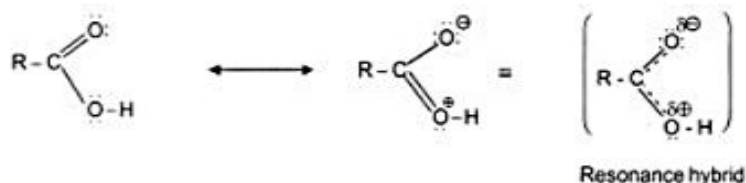


# CARBOXYLIC ACID & ITS DERIVATIVES

## GENERAL INTRODUCTION

The organic compounds containing carboxyl ( $\text{-}\overset{\text{O}}{\parallel}\text{C}\text{-OH}$ ) group are known as carboxylic acids and the term 'Carboxylic' was firstly proposed by scientist 'Bayer'.

Resonance hybrid structure of carboxylic acid group is



## Classification

On the basis of the group to which  $\text{-COOH}$  group is attached.

(a) Aliphatic carboxylic acid =  $\text{R}-\overset{\text{O}}{\parallel}\text{C}-\text{OH}$  (R = H atom or alkyl group).

(b) Aromatic carboxylic acid =  $\text{Ar}-\overset{\text{O}}{\parallel}\text{C}-\text{OH}$  (Ar = Aryl group)

On the basis of number of  $\text{-COOH}$  groups in their molecule.

	No. of $\text{-COOH}$ group
(a) Mono carboxylic acids	1
(b) Dicarboxylic acids	2
(c) Tricarboxylic acids	3

General formula is  $\text{C}_n\text{H}_{2n}\text{O}_2$  or  $\text{C}_n\text{H}_{2n+1}\text{COOH}$

Saturated and unsaturated mono carboxylic acids are also called fatty acids, because higher acids like palmitic acid, stearic acid, oleic acid, etc. were obtained by hydrolysis of fats and oils.

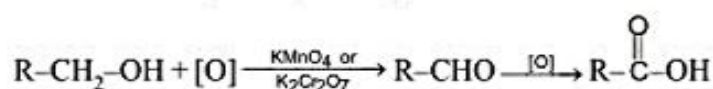
Isomerism – Chain, positional, functional group and optical.

Hybridisation state of C in the carboxyl group is  $\text{sp}^2$

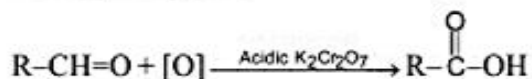
## METHOD OF PREPARATION

By the oxidation of alcohols, aldehydes and ketones :

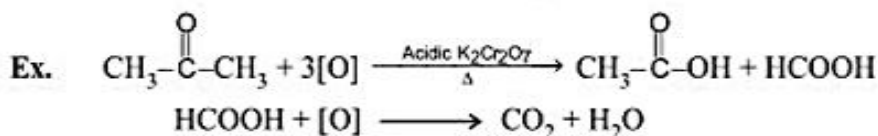
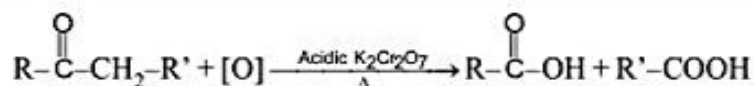
(a)  $1^\circ$  Alcohol  $\xrightarrow{[\text{O}]}$  corresponding carboxylic acids.



(b) Aldehyde  $\xrightarrow{[O]}$  corresponding acids

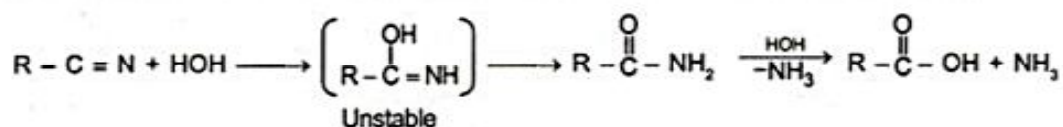


(c) Ketones  $\xrightarrow{[O]}$  mixture of acids of lesser no. of C atoms than the ketone.



**By the hydrolysis of cyanides (nitriles) :**

Cyanides on complete hydrolysis in the presence of dilute HCl form carboxylic acids.



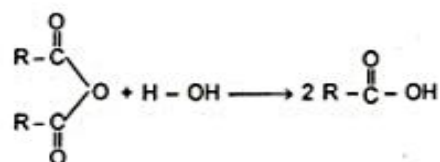
**From hydrolysis of acid derivatives :**



(a) **From acyl halides :**



(b) **From acid anhydride :**



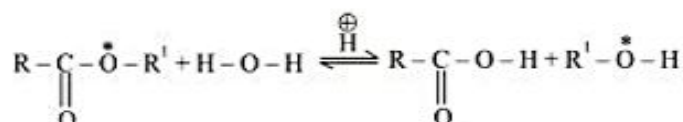
**Note :** Formic acid cannot be prepared by these two reactions (a & b) because its corresponding formyl chloride and formic anhydride are unstable compounds.

(c) **From carboxylic ester (Hydrolysis of Ester) :**

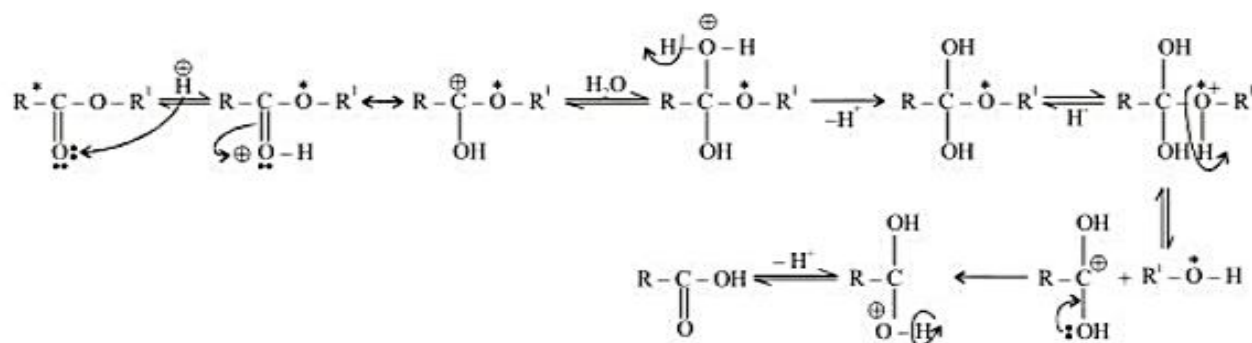
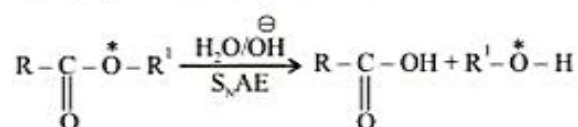
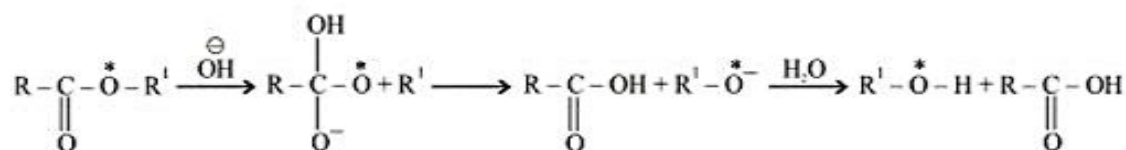
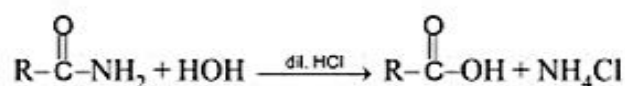
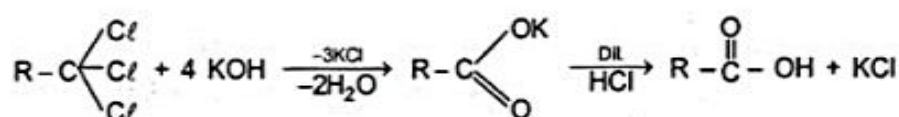


Hydrolysis of ester possible in acidic medium as well as in basic medium.

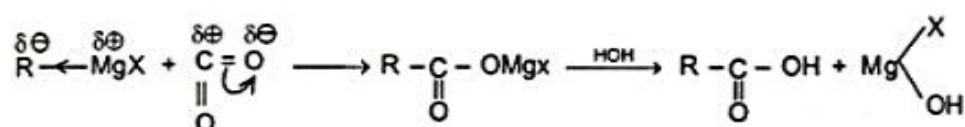
(i) **Hydrolysis in acidic medium :**





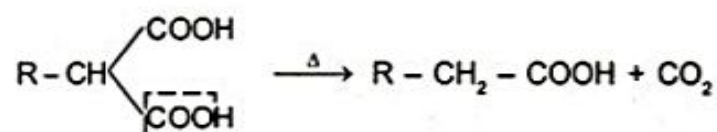
**Mechanism :****(ii) Hydrolysis in basic medium :****Mechanisms :****(d) From acid amides :****By alkaline hydrolysis of alkylidene trihalides :****From carboxylation of grignard's reagent :**

By passing  $\text{CO}_2$  in ether Solution of Grignard's reagent

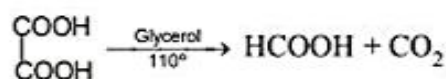


**Note :** Formic acid can not be prepared by this method.

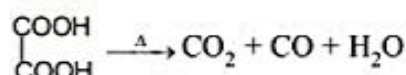
### Partial decarboxylation of gem dicarboxylic acids :



**Note :** Formic acid is prepared from oxalic acid (laboratory method) by heating at about  $110^\circ$  in the presence of glycerol.

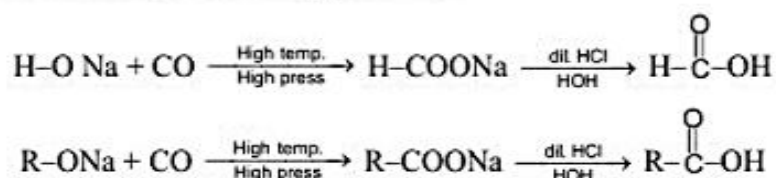


In absence of glycerol

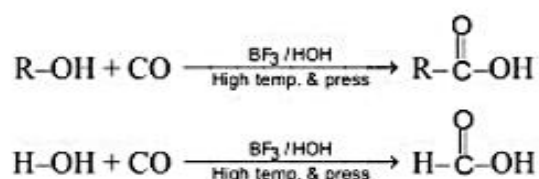


### Carboxylation of :

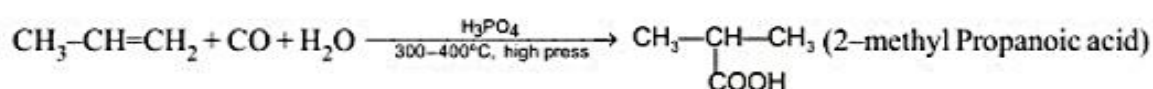
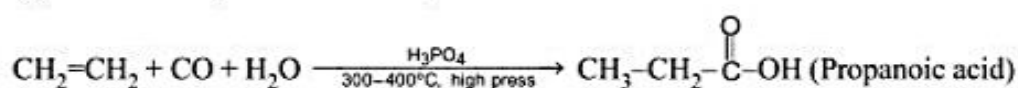
#### (a) Sodium alkoxides or sodium hydroxide :



#### (b) Alcohols :

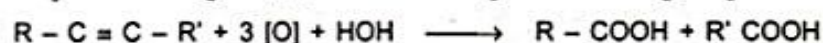
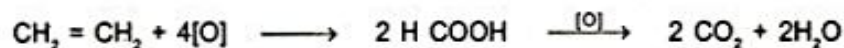
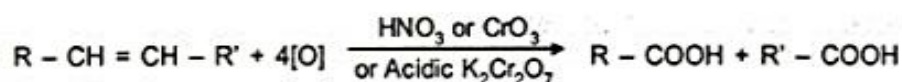


#### (c) Alkenes [Koch Reaction] :



**Note :** Formic acid and acetic acid can not be prepared by this method.

### Oxidation of alkenes and alkynes :

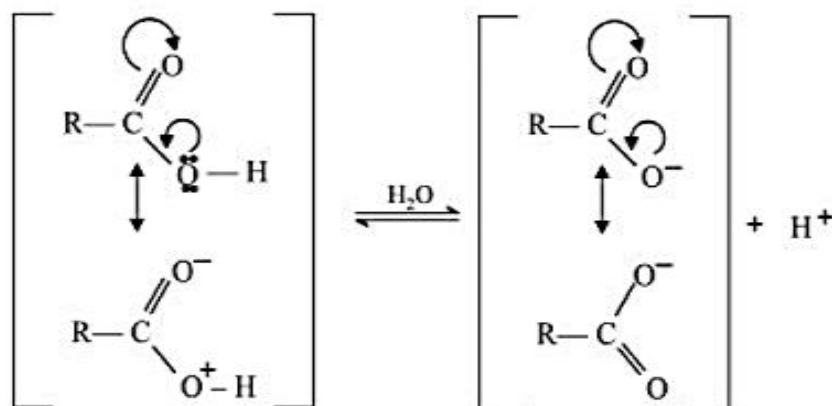




## CHEMICAL PROPERTIES

### Acidic Nature

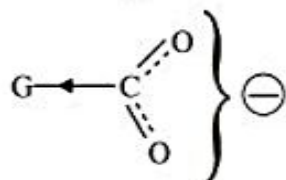
Carboxylic acids are weakly acidic ( $K_a$  values are of the order  $10^{-4}$  to  $10^{-5}$ ) but a measurable equilibrium exists between acids and ions.



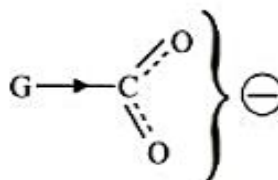
Both the acid and anion are resonance stabilised, but stabilisation is more powerful between exactly equivalent resonating structures of the carboxylate ion.

### Effect of Substituents on Acidity

Electron-withdrawing groups disperse the negative charge on the carboxylate ion, thereby stabilising it and increasing the acidity. Electron-donating groups intensify the negative charge, thereby destabilising the carboxylate ion and decreasing the acidity.



G withdraws electrons: stabilises anion, strengthens acid



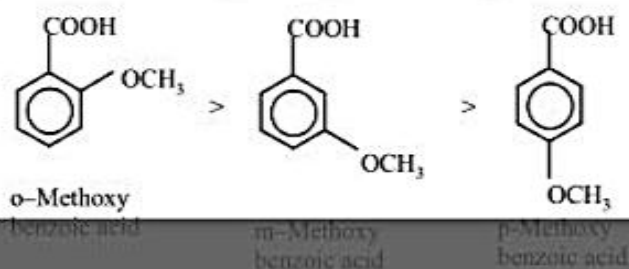
G releases electrons: destabilises anions, weakens acid.

For example, chloroacetic acid is hundred times stronger than acetic acid.

The effect of substituents on acidic strength of benzoic acids is the same. For example, benzoic acid is stronger than p-methoxybenzoic acid but weaker than p-nitrobenzoic acid. (Methoxy group is electron-releasing whereas nitro group is electron-withdrawing.)

### Ortho Effect

Among isomeric substituted benzoic acids, ortho-isomer is the strongest acid irrespective of the nature of substituent. Example: The acidic strength among the following acids is of the order



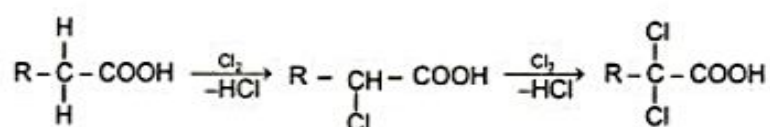


Carboxylic acids give following reactions :

1. Due to alkyl group
2. Due to acidic hydrogen
3. Due to  $>C=O$  group
4. Due to  $-OH$  group
5. Due to  $-COOH$  group
6. Special reaction of alcanoic acid

**(1) Reactions due to alkyl group :**

**Halogenation :** Acids having  $\alpha$ -H atom give this reaction. The  $\alpha$ -H atoms are easily replaced by chlorine or bromine atoms, forming halogen derivatives of acids.

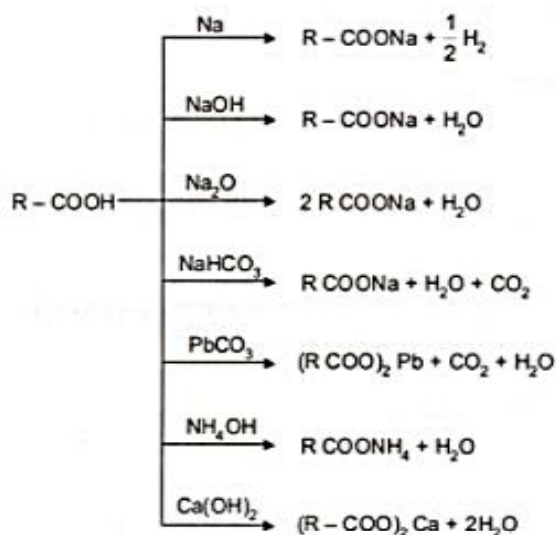


- Note :** (i) The reaction is known as hell-volhard-Zelinisky (HVZ) reaction.  
 (ii) In the presence of phosphorus, monohalo product is formed as the main product.  

$$\text{R}-\text{CH}_2-\text{COOH} + \text{Br}_2 \xrightarrow{\text{P}} \text{R}-\text{CH}(\text{Br})-\text{COOH} + \text{HBr}$$
  
 (iii) Formic acid does not show HVZ reaction due to absence of alkyl group or  $\alpha$ -H atom.

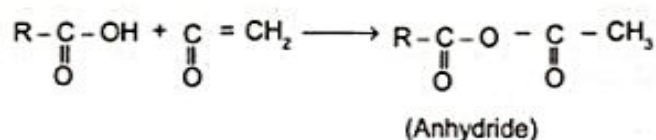
**(2) Due to acidic hydrogen :**

- (a) Salt Formation :** Carboxylic acids form salts with metals, metal oxide, hydroxides, carbonates, bicarbonates and compounds showing basic nature.

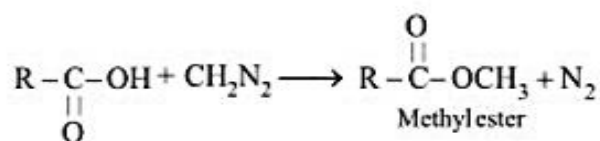


**Note :** Acids liberate  $\text{CO}_2$  with  $\text{NaHCO}_3$ . This reaction is used to distinguish carboxylic acid from phenol which does not react with  $\text{NaHCO}_3$ .

**(b) Reaction with Ketene :**

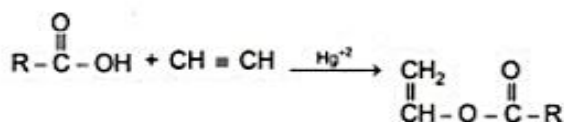
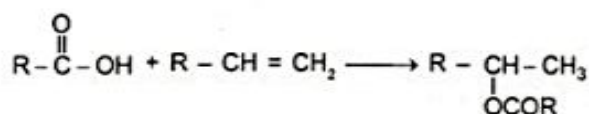
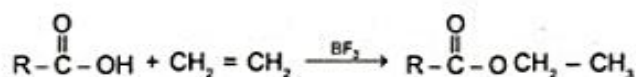
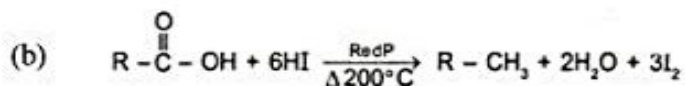
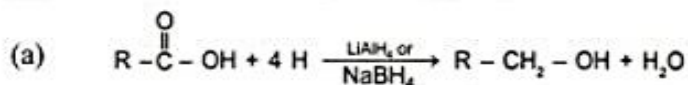
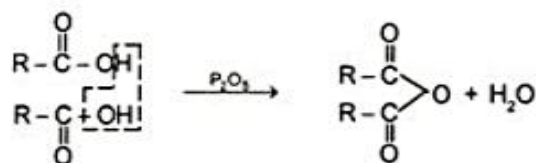


## (c) Reaction with diazomethane :

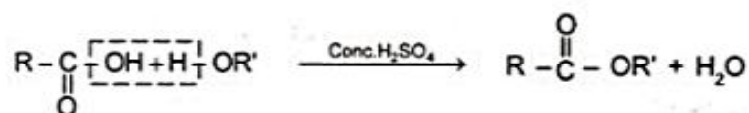


**Note :** Diazomethane is a powerful methylating agent. So by this method methyl ester can be prepared.

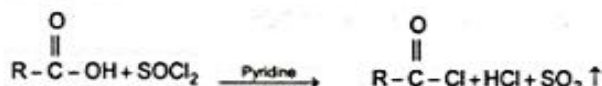
## (d) Reaction with alkene and alkyne :

(3) Reaction due to ( $>\text{C}=\text{O}$ ) group :(4) Reactions due to ( $-\text{OH}$ ) group :(a) With  $\text{P}_2\text{O}_5$  (Dehydrations)

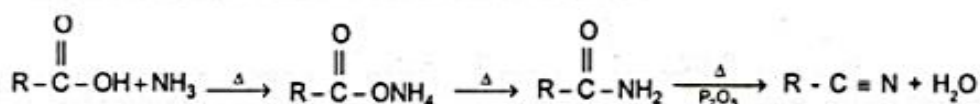
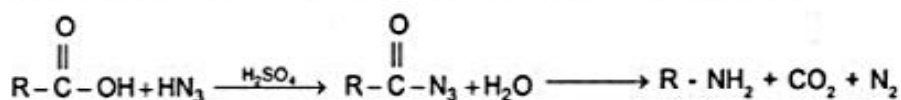
## (b) Esterification :



**Note :** The reaction is proton-catalysed esterification. In the reaction OH comes from the acid and H from the alcohol for release of  $\text{H}_2\text{O}$ .

(c) **Reaction with Phosphorus Chlorides :**(d) **With Thionyl Chloride :**

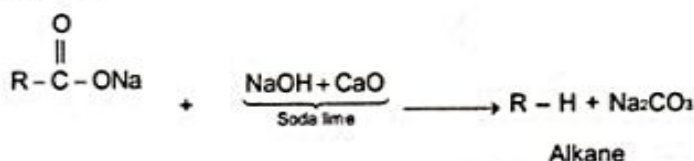
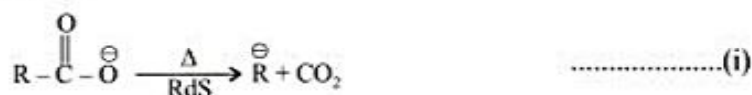
**Note :** In the reaction  $\text{SO}_2$  is gas so escapes out and  $\text{HCl}$  is an acid, gets absorbed by basic pyridine and pure acyl chloride is left. So its is best method for preparing acyl chloride from acids.

(e) **Formation of acid Amides and Alkane Nitriles :**(f) **With Hydrazoic acid (Schmidt reaction) :  $\text{N}_3\text{H}$  = Hydrazoic acid**

The reaction is a modification of "curtius reaction".

(5) **Reaction due to  $(-\text{COOH})$  group :**(a) **Decarboxylation of Carboxylic Acids**

On heating carboxylic acids with soda-lime ( $\text{NaOH}$  and  $\text{CaO}$ ), an alkane is obtained with one carbon less than the carboxylic acids.

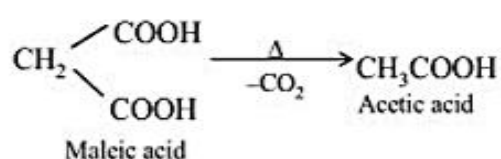
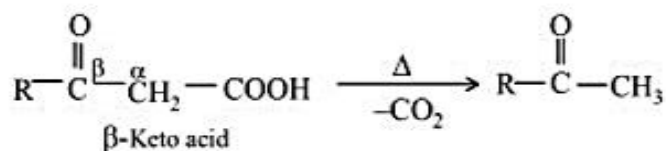
**Mechanisms :**

**Note :-**

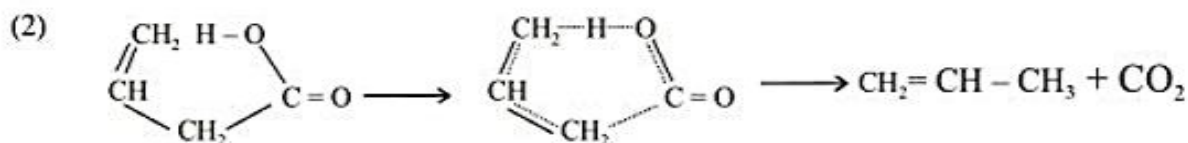
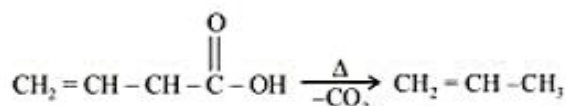
- (i) Step I<sup>st</sup> is reversible but presence of CaO shift the equilibrium in the formed direction.  

$$\text{CaO} + \text{CO}_2 \longrightarrow \text{CaCO}_3$$
- (ii) Step I<sup>st</sup> is RdS i.e. formation of carbanion
- (iii) Rate of decarboxylation is directly proportional to stability of carbanion.

**$\beta$ -keto acid :**  $\beta$ -Keto acids decarboxylate readily when heated to a temperature of  $100^\circ\text{C} - 150^\circ\text{C}$ .

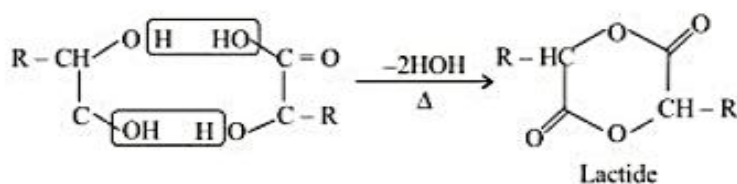


- (1)  $\beta$ - $\gamma$  unsaturated carboxylic acid gives alkene on simple heating.

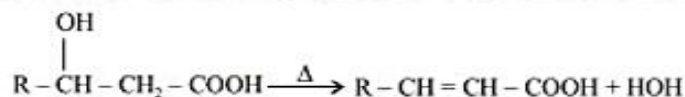


### Heating effect

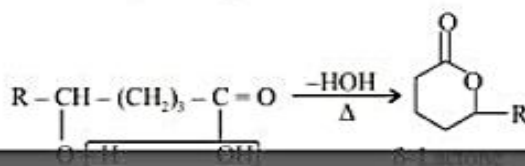
**$\alpha$ -Hydroxy acid :**  $\alpha$ -hydroxy acids on heating form lactide. Reaction takes place between two moles of acid.



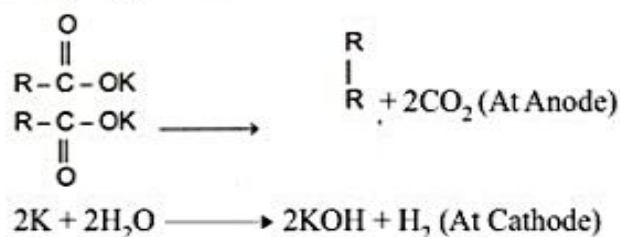
**$\beta$ -Hydroxy acid :**  $\beta$ -hydroxy acids on heating undergo dehydration to give  $\alpha, \beta$  unsaturated acids.



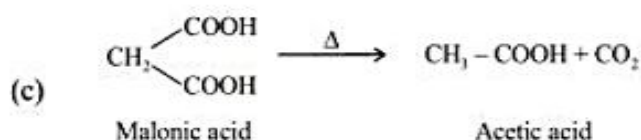
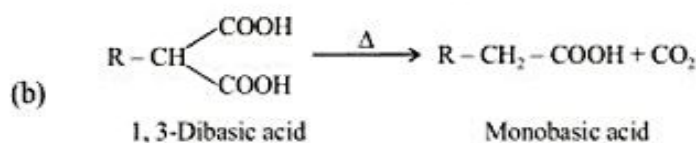
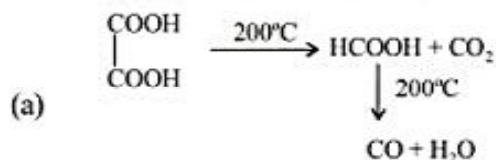
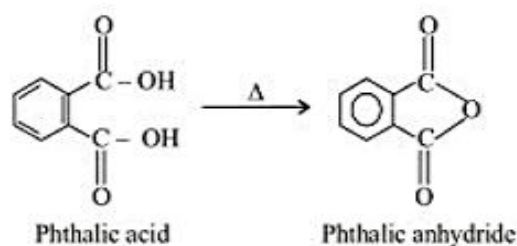
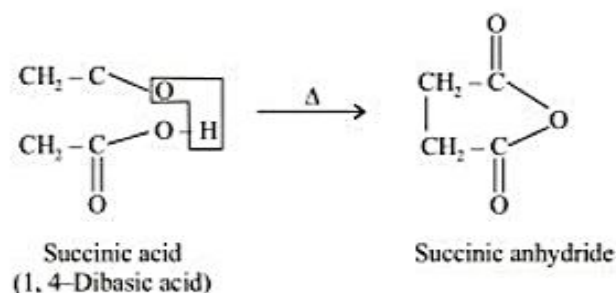
**$\gamma$ -and higher hydroxy acids :** They form cyclic ester known as lactones.

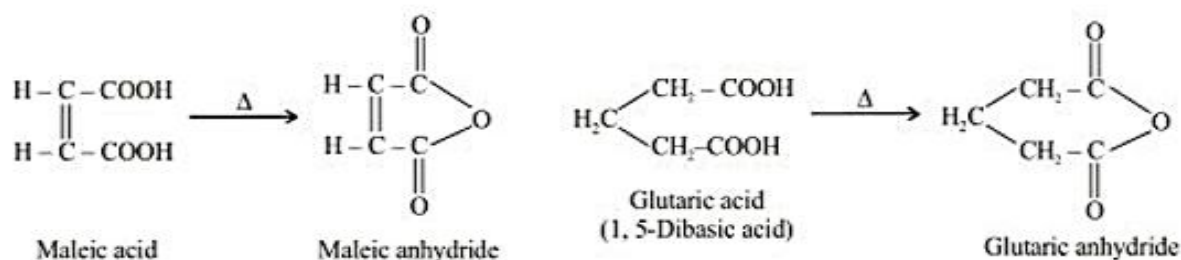




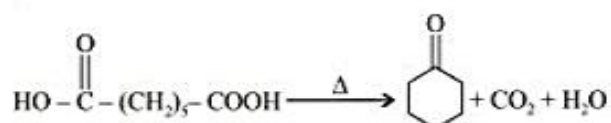
(b) **Kolbe's electrolytic synthesis :****Action of heat or dehydrating agents on dibasic acids**

Variety of products are obtained when dicarboxylic acids are heated. The nature of product depends on the carbon chain length separating the two carboxylic groups.

(1) **1, 2 and 1, 3-dibasic acids undergo decarboxylation to form monobasic acids.**(2) **1, 4 and 1, 5-dibasic acid undergo intramolecular dehydration to give cyclic anhydrides.**

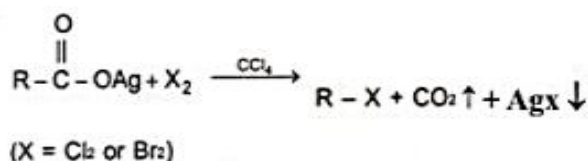


- (3) **1, 6 and 1-7dibasic acid :** These two acids undergo dehydration as well as decarboxylation to give cyclic ketones. 1, 6-Dibasic acids give cyclopentanone and 1, 7-dibasic acids give cyclohexanone.



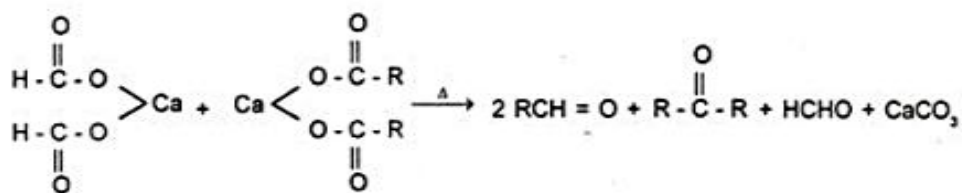
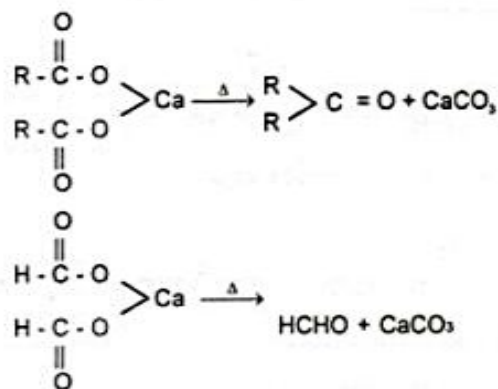
**Note :** Kolbe synthesis undergoes free radical mechanism.

(c) **Hunsdiecker reaction :**

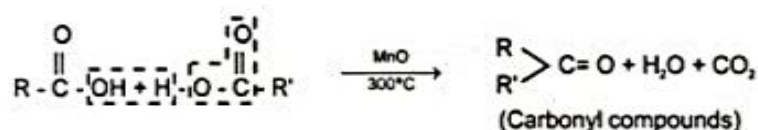


**Note :** In the reaction decarboxylative halogenation of the acid takes place. The reaction is useful in stepping down a homologous series.

(d) **Formation of carbonyl compounds [Dry distillation of calcium salt] :**



(e) **With Manganous oxide :**

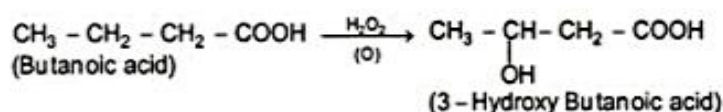


(5) **Special reaction of alkanolic acid :**

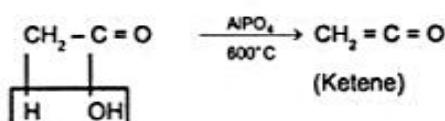
(a) **Oxidation :**

→ By  $\text{SeO}_2$   $\alpha$  keto acid is formed

→ By  $\text{H}_2\text{O}_2$  -OH group comes at  $\beta$  -C atom.



(b) **Pyrolysis :**



## SPECIAL FEATURES OF FORMIC ACID

(a) Formic acid shows acidic character due to the presence of  $-\text{COOH}$  group as well as shown reducing character due to the presence of  $-\text{CHO}$  group.



(b) It reduces Tollen's reagent and forms silver mirror.

(c) It reduces mercuric chloride and forms black ppt. of mercury.

(d) It decolourises the pink colour of acidic  $\text{KMnO}_4$

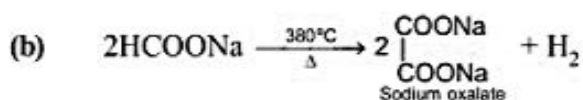
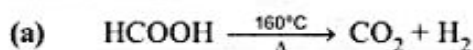
(e) It forms brown ppt. of  $\text{MnO}_2$  with basic  $\text{KMnO}_4$

(f) It converts the orange colour of acidic  $\text{K}_2\text{Cr}_2\text{O}_7$  into green colour.

(g) It reduces Fehling solution.

(h) Dehydration  $\text{HCOOH} \xrightarrow[\text{Conc. H}_2\text{SO}_4]{\Delta} \text{H}_2\text{O} + \text{CO}_2$

(i) **Effect of heat :**

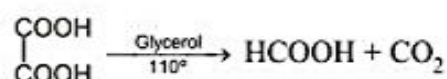


## DISTINCTION BETWEEN FORMIC ACID AND ACETIC ACID

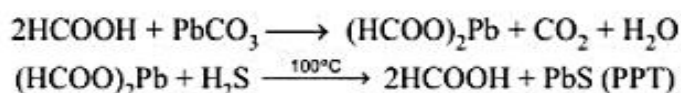
S.No.	HCOOH	CH <sub>3</sub> COOH
1.	Decomposed on heating to give carbon dioxide and hydrogen	Stable
2.	With concentrated sulphuric acid gives carbon monoxide and water	Stable
3.	With halogen, there is not action	Substituted acids are formed.
4.	Reduces ammonical silver nitrate and Fehling's solution	No action
5.	Calcium salt on heating gives formaldehyde	Calcium salt on heating gives acetone
6.	Sodium salt on heating gives sodium oxalate hydrogen	No action
7.	Sodium salt + Soda lime gives hydrogen	Methane is produced
8.	Electrolysis of alkali solution gives hydrogen	Ethane is obtained
9.	Decolourises acidified KMnO <sub>4</sub> solution	No action
10.	Dichromate solution turns into green coloured solution	No action

### FORMIC ACID (HCOOH)

#### 1. Lab Reaction :



**Note :** BP of HCOOH is 100.5°, for removal of water from formic acid we can use PbCO<sub>3</sub> or PbO (Litharge) and H<sub>2</sub>S.



#### 2. Industrial method :

It is prepared on large scale by reaction CO with aqueous sodium hydroxide under pressure 1 atm and 473 K



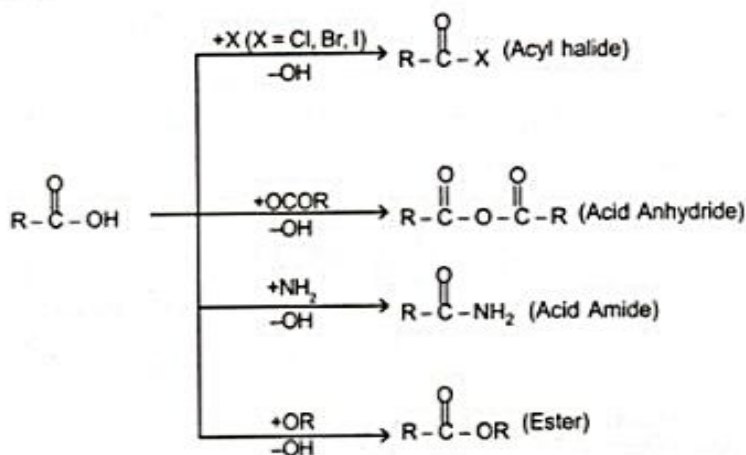




## ACID DERIVATIVES

### GENERAL INTRODUCTION

Replacement of  $-OH$  group of the  $-COOH$  group in a carboxylic acid by an atom or by any other functional group give rise to certain new families of compounds. These compounds are called acid derivatives.

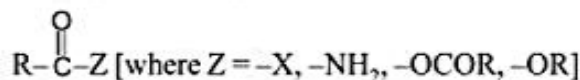


Acyl chlorides are the most important acid halides. The first member of this family is acetyl chloride because formylchloride is unstable.

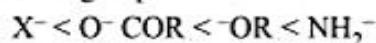
Similarly acetic anhydride is the representative member of the acid anhydrides family, because formic anhydride is unstable.

The first two members of Acid Amide family are formamide and Acetamide. Acetamide is an important acid amide.

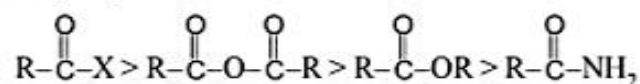
Esters have functional group isomerism with acids.



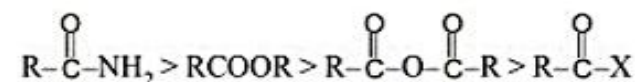
\* Order of basic character of group Z



\* Reactivity order/Rate of hydrolysis



\* Order of stability

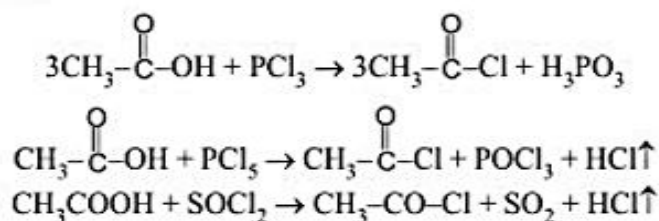


Derivatives regenerate the parent acid on hydrolysis.

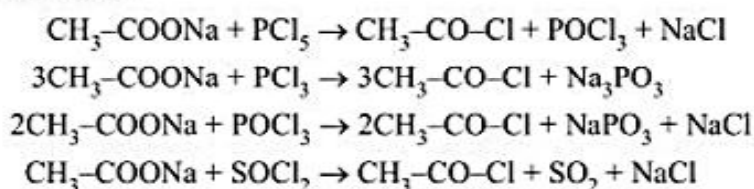
## ACETYL CHLORIDE $[\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{Cl}]$

Method of preparation :

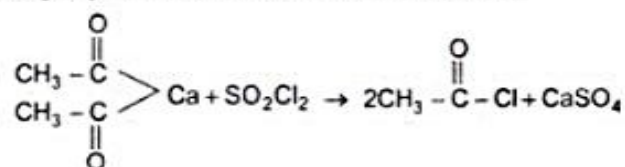
Laboratory method :



From Sodiumacetate :



By the reaction of sulphuryl chloride on calcium ethanoate :



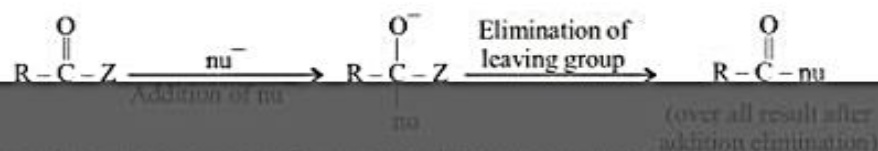
Physical Properties :

- (i) Colourless liquid, having pungent odour.
- (ii) Slowly soluble in water, soluble in organic solvents like  $\text{CHCl}_3$ ,  $\text{CCl}_4$ ,  $\text{CH}_3-\text{CO}-\text{CH}_3$ , etc.
- (iii) Produces blister on skin and its vapour causes irritation in eyes.
- (iv) Boiling point is  $51^\circ\text{C}$ .
- (v) Fumes strongly in moist air.

**$\text{S}_{\text{NAE}}$  Reaction :** If attacking reagent is nucleophile then most of the reaction of acid derivative (besides  $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}_2$ ) take place via  $\text{S}_{\text{NAE}}$  mechanism.  $\text{S}_{\text{NAE}}$  stands for nucleophilic addition elimination substitution reaction.

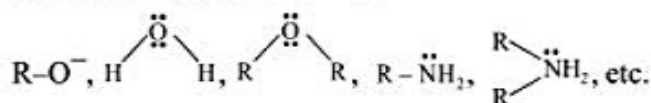


Mechanisms :



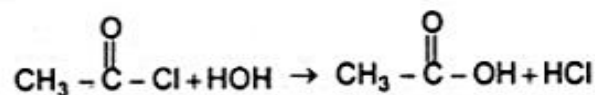
Here

Note :  $\text{nu}^-$  may be  $\text{OH}^-$ ,  $\text{NH}_2^-$

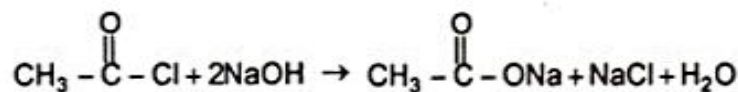


**Chemical properties :**

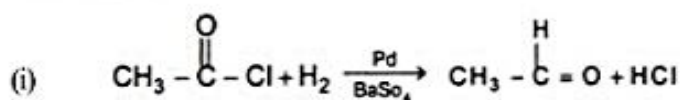
(1) **Hydrolysis :**



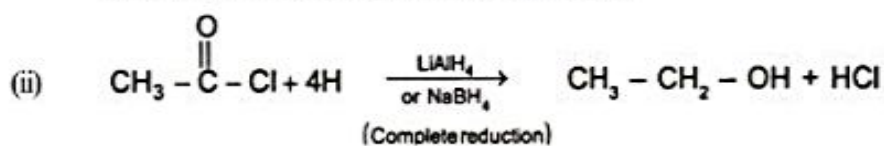
on alkaline hydrolysis



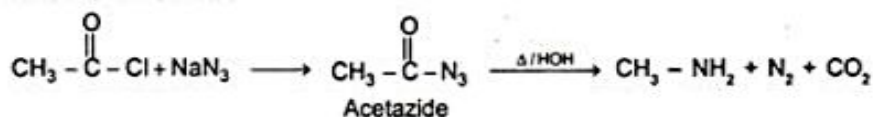
(2) **Reduction :**



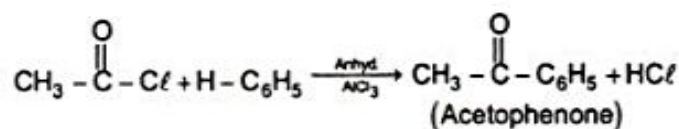
(Rosenmund's reduction, partial reduction)



(3) **Curtius Reaction :**



(4) **Friedel Craft's reaction :**

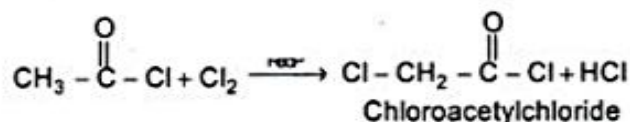


(5) **With Grignard's reagent :**

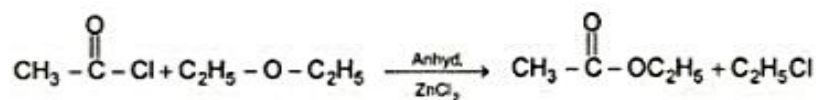




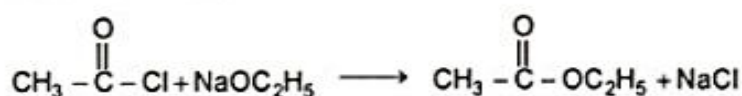
## (6) Halogenation :



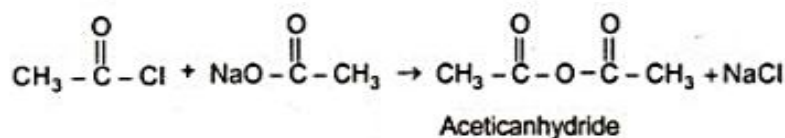
## (7) With Ether :



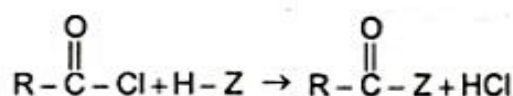
## (8) With Sodium Ethoxide :



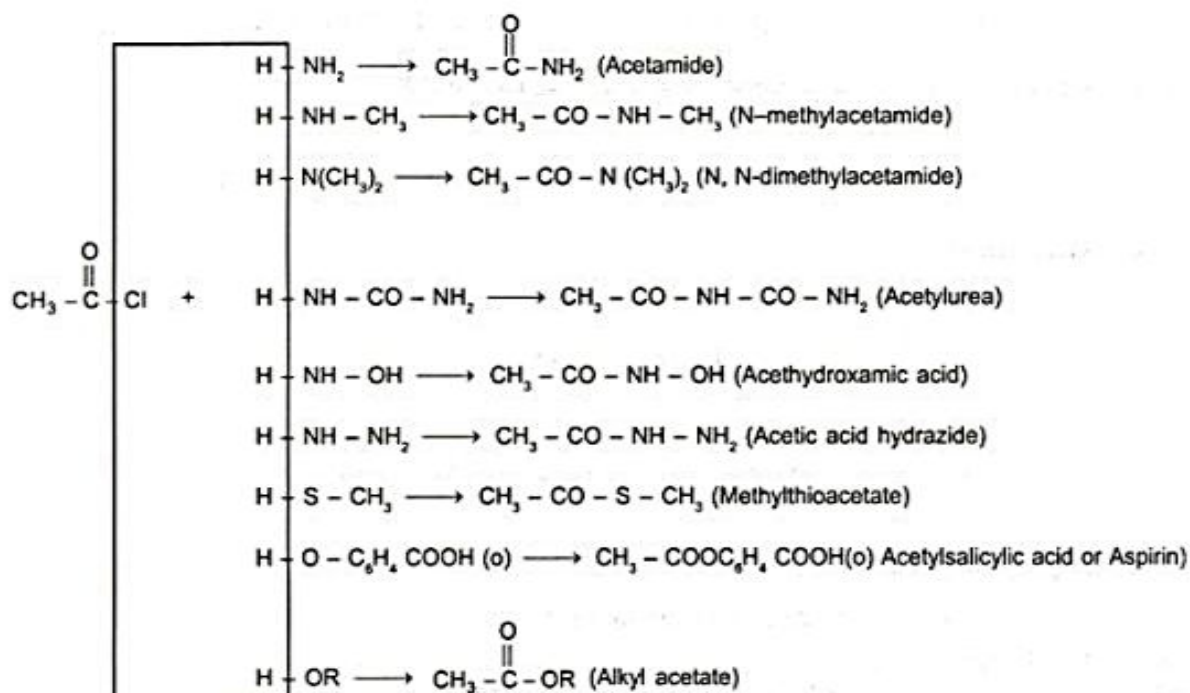
## (9) With Sodium Acetate :



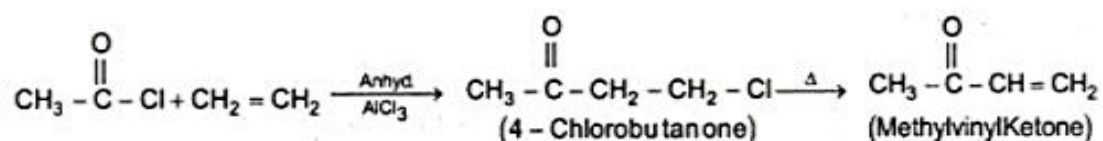
## (10) Acetylation of Compounds having reactive hydrogen atom :



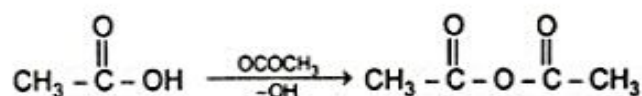
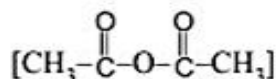
Ex.



(11) With Alkene :

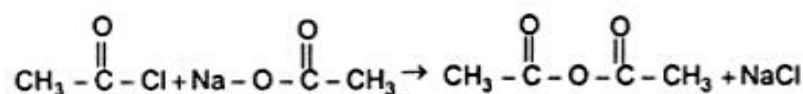
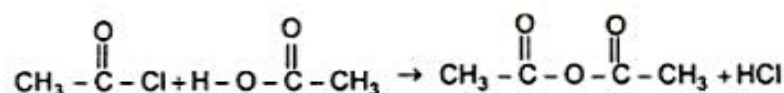


## ACETIC ANHYDRIDE



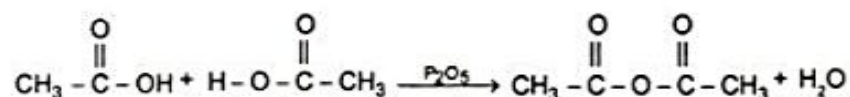
(I) Method of preparation :

From Acetyl chloride :

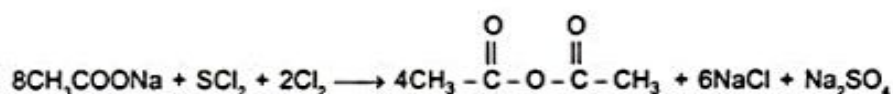


(Laboratory Method)

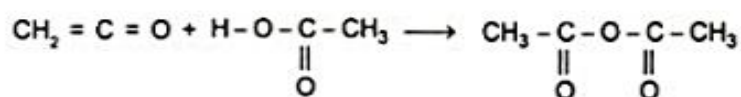
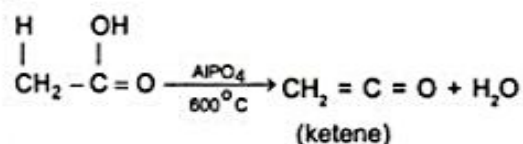
From Acetic acid :



By passing chlorine in a mixture of  $\text{SCl}_2$  and sodium acetate :

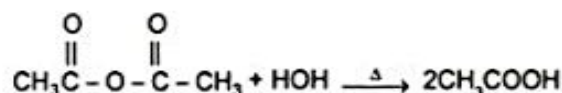
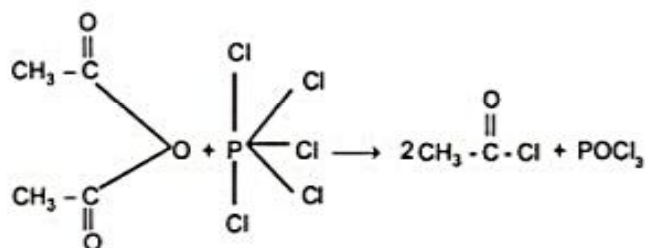
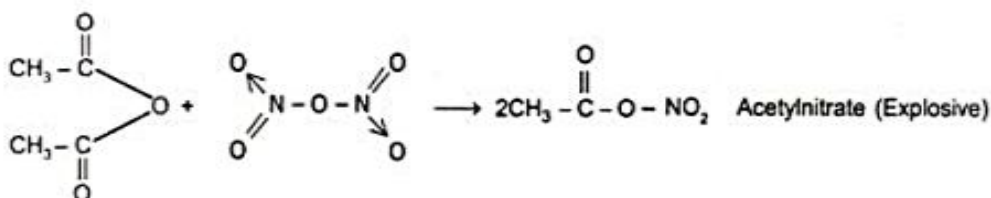
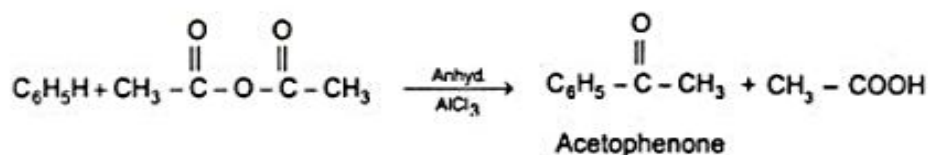
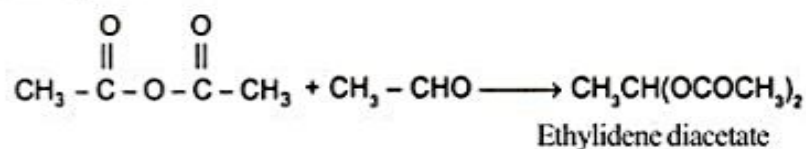


From Ketene :

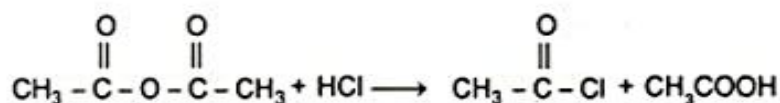


**(2) Physical Properties :**

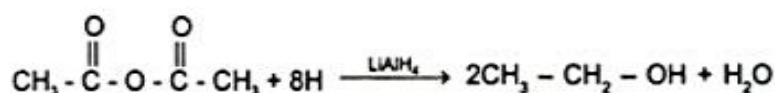
- (i) It is colourless liquid having pungent vinegar like odour.
- (ii) Boiling point is 138°C.
- (iii) Slowly soluble in cold water, but readily soluble in hot water

**(3) Chemical Properties :****Hydrolysis :****With  $\text{PCl}_5$  :****With  $\text{N}_2\text{O}_5$  :****With Benzene [Friedel–Craft's Reaction] :****With Acetaldehyde :**

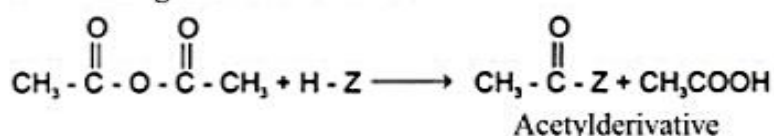
With Dry HCl gas :



Reduction :

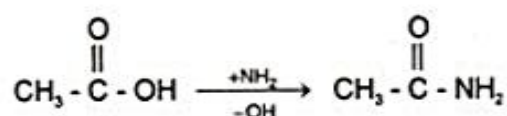
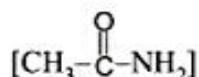


With Compounds having reactive H-atom :



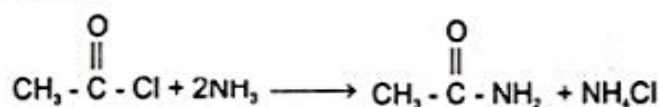
**Note :** Products are similar as in case of Acetyl chloride.

## ACETAMIDE

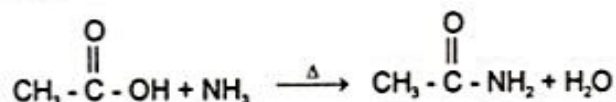


### (1) Method of Preparation :

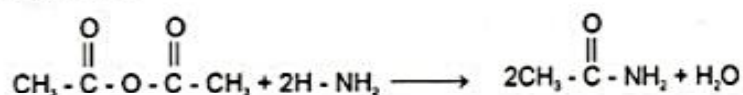
From Acetylchloride :



From Acetic Acid :



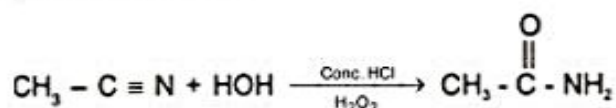
From acetic Anhydride :



From Ethyl Acetate :

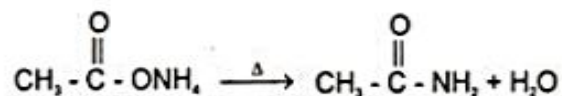


Partial hydrolysis of Acetonitrile :





By thermal decomposition of Ammonium acetate :

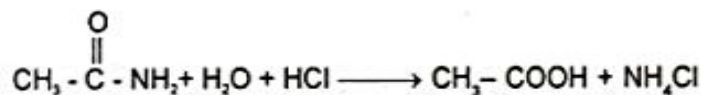


(2) **Physical properties :**

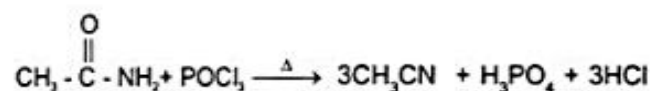
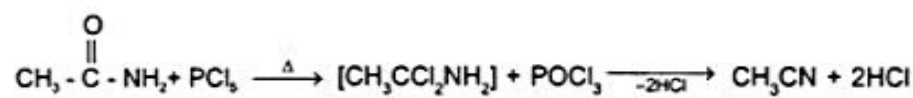
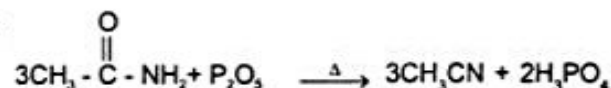
- (i) It is a hygroscopic white crystalline solid.
- (ii) It has faint smell in pure state, but a rat like smell in impure state.
- (iii) It is soluble in water and alcohol, but sparingly soluble in ether.
- (iv) Melting point  $82^\circ\text{C}$  and boiling point is  $222^\circ\text{C}$ .

(3) **Chemical properties :**

**Hydrolysis :**

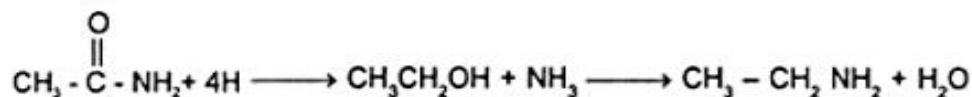


**Dehydration :**



**Reduction :**

Reducing Agent : Metal Catalyst +  $\text{H}_2$ , Na + Ethanol,  $\text{LiAlH}_4$  etc.

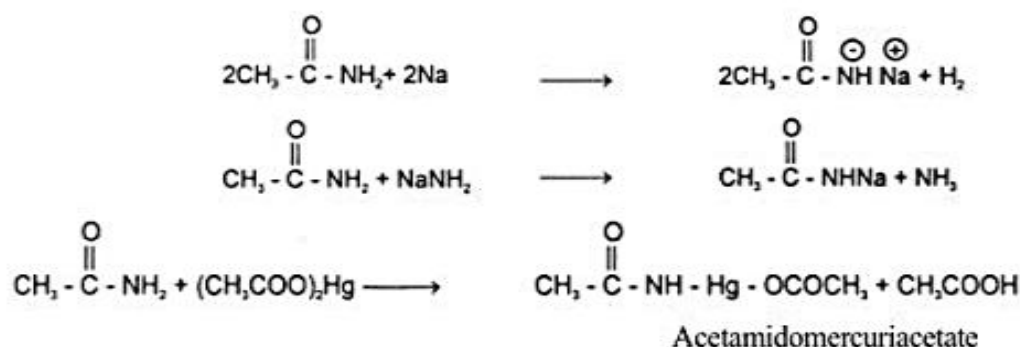
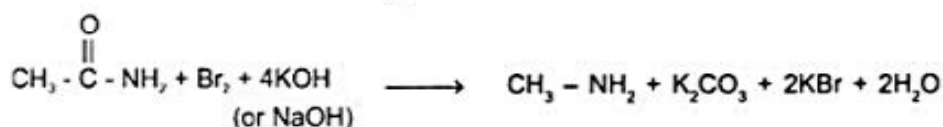


**With Nitrous Acid :**

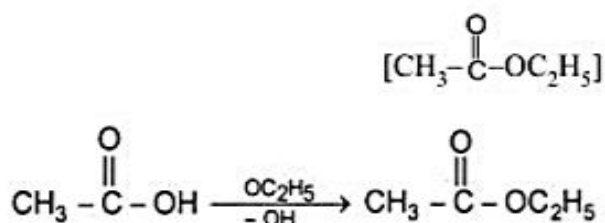
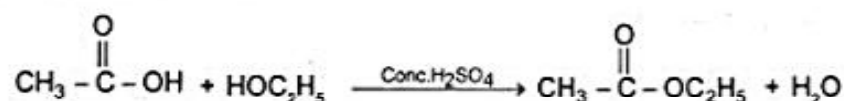
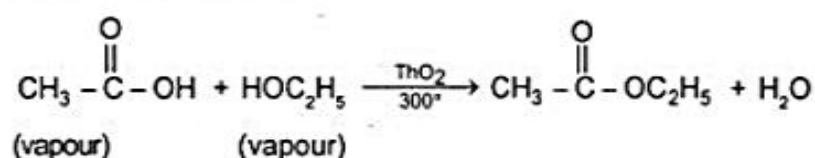


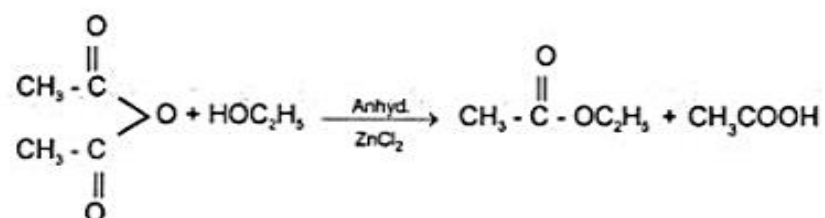
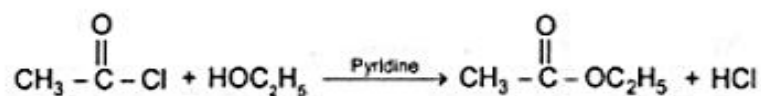
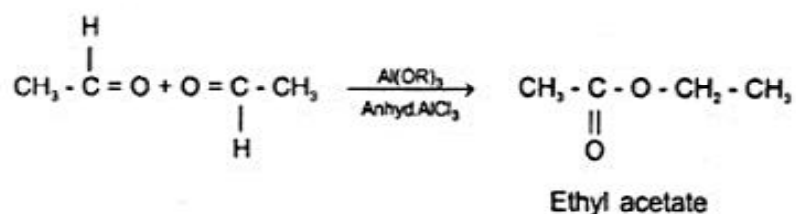
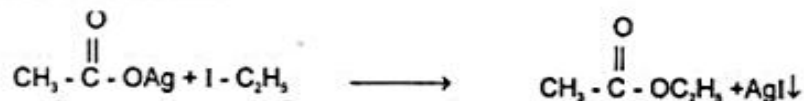
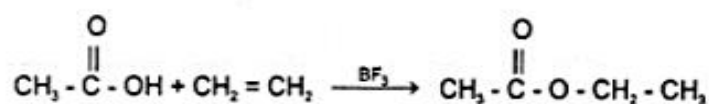
**Amphoteric character :**

Acetamids forms salts on reacting with strong bases as well as strong acids. Therefore it behaves like a weak base as well as weak acid. i.e. it shows amphoteric character.

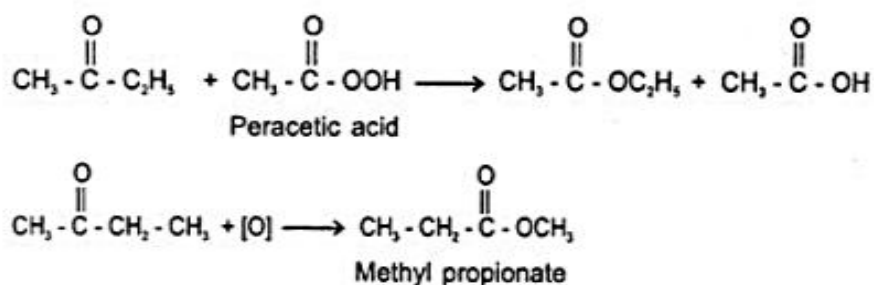
(i) **Weak acidic behaviour :**(ii) **Weak basic behaviour :****Hofmann Bromamide Reaction or Hypobromite Reaction :**

**Note :** In the reaction decrease of one carbon atom takes place. Therefore it can be used in descending down a homologous series and it is also called Hofmann degradation.

**ETHYL ACETATE AND ACETIC ESTER****(1) Methods of preparation :****By liquid phase Esterification :****By vapour phase Esterification :**

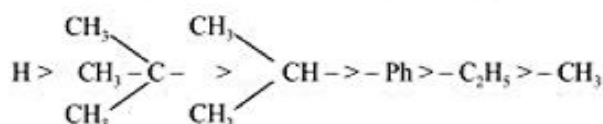
**By Aacylation of Ethanol :****Tischenko Reaction :****Ethylation of Silver halides :****Ethanolysis of Ethanenitrile :****By addition of Acetic acid on Ethylene :****By reaction of sodium Ethoxide on Acetyl chloride :****Baeyer-Villiger Oxidation :**

Ethyl acetate is formed on reacting butanone with a peracid, Methyl propionate is also formed in small amounts.



**Note : (Direct approach)**

- (I) In Baeyer villiger oxidation 'O' is inserted between  $-\overset{\text{O}}{\parallel}\text{C}$  & alkyl group.
- (II) If alkyl groups are different then 'O' is inserted between  $-\overset{\text{O}}{\parallel}\text{C}$  & that alkyl group which has greater migratory aptitude.
- (III) Order of migratory aptitude in Baeyer villiger Oxidation is

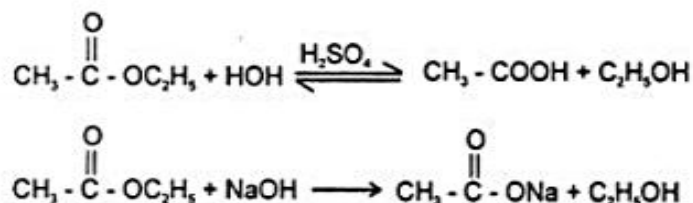


**(2) Physical Properties :**

- (i) Colourless, sweet smelling steamvolatile, inflammable liquid.
- (ii) Very sparingly soluble in water, but soluble in organic solvents.
- (iii) Boiling point  $78^\circ$ .

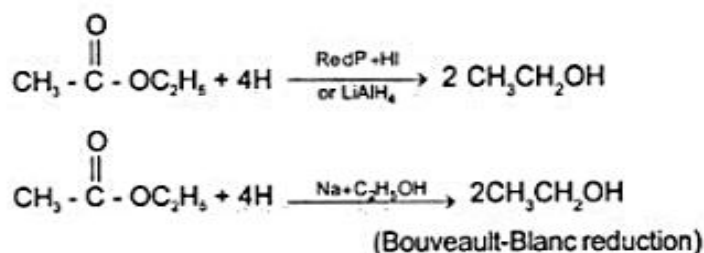
**(3) Chemical Properties :**

**Hydrolysis :**

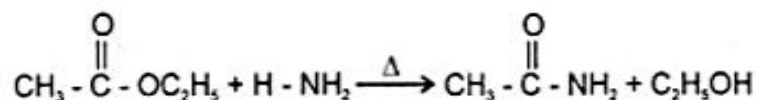
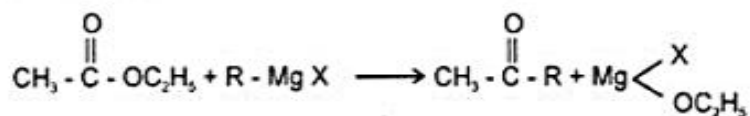


**Note :** In esters caustic alkalies hydrolysis is rapid and complete. Alkaline hydrolysis of esters is called "Saponification".

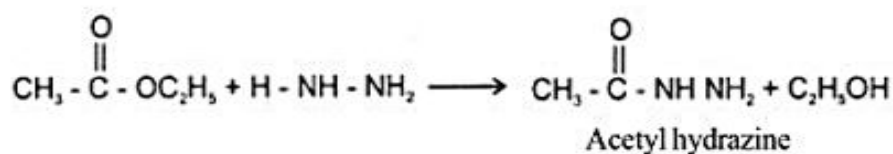
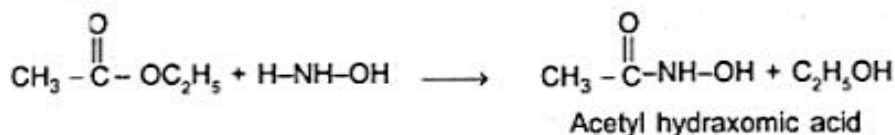
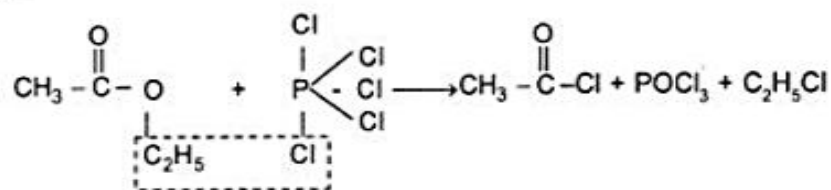
**Reduction :**



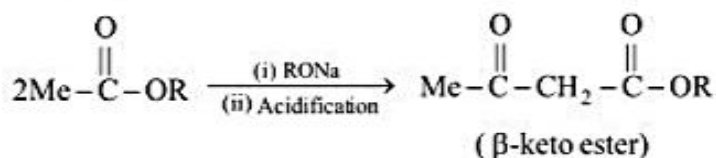


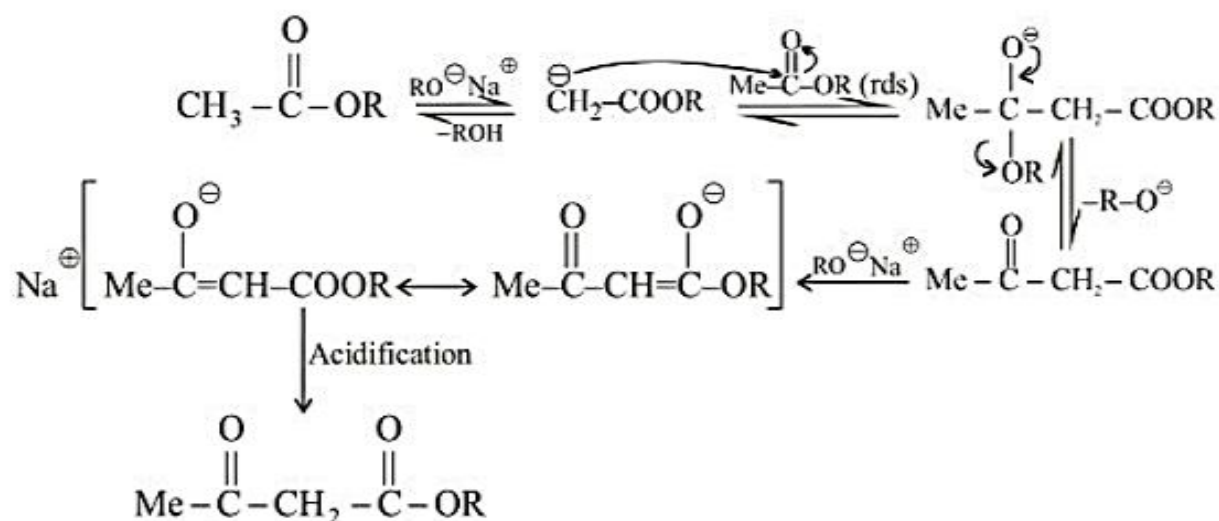
**Ammonolysis :****With Grignard's Reagent :**

**Note :** The product will be tertiary alcohol when 2 mole of Grignard's reagent are taken.

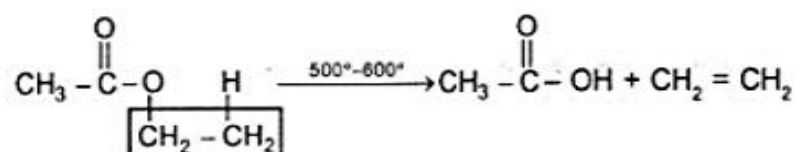
**With Hydrazine :****With Hydroxyl Amine :****With  $\text{PCl}_5$  :****Claisen ester Condensation**

Esters undergo  $\text{S}_{\text{N}}\text{AE}$  Reaction, when attacked by a  $\text{Nu}^\ominus$  generated by the interaction of a base (usually base related to the Alkoxy anion of ester) with one of the molecule of ester and this  $\text{Nu}^\ominus$  attacks on another molecule. The reaction over all is considered as condensation of esters known as claisen ester condensation.

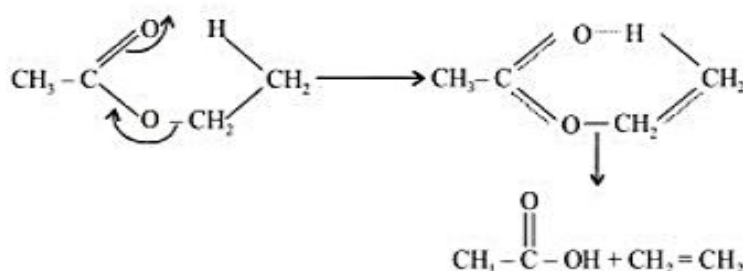
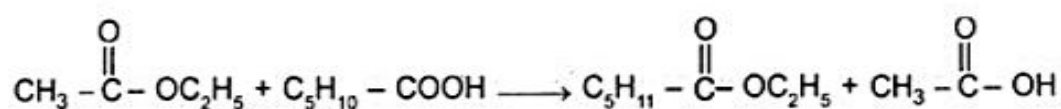


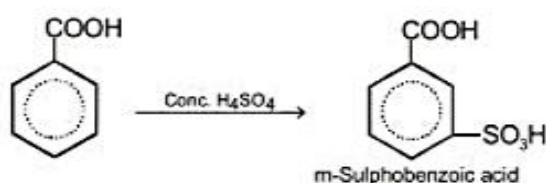
**Mechanism :**

Some times, when two ester groups are present within the molecule then the condensation occurs intramolecular then cyclization caused thus is known as Dieckmann cyclization or Dieckmann's condensation.

**Pyrolysis or Thermal decomposition :****Mechanisms**

Reaction takes place via 6 membered cyclic transition state

**Acidolysis :**



**Note :** Due to the presence of a deactivating m-directing COOH group in benzoic acid, the latter does not give Friedel–Crafts reaction.

## (5) Tests

### 1. Formation of Ferric salt :

A red–brown precipitate is obtained on adding a small amount of neutral ferric chloride solution in benzoic acid solution.

### 2. Esterification :

A sweet odour of ethyl benzoate is perceived on heating benzoic acid after adding a few drops of ethyl alcohol and concentrated sulphuric acid.

### 3. Decarboxylation :

Inflammable vapours of benzene are liberated out on heating benzoic acid after mixing it thoroughly with soda lime.

## (6) Uses

**Benzoic acid is used as follows :**

1. As a germicide.
2. Benzoic acid and its salts are used in the form of medicines.
3. Sodium benzoate is used as a preservative of canned food products.
4. Benzoic acid is used in the manufacture of many synthetic dyes, like aniline blue dye.
5. Ethyl ester of benzoic acid (ethyl benzoate) is used as a flavouring agent.

## BENZOIC ACID

### BENZOIC ACID ( $C_6H_5COOH$ )

Benzoic acid was first obtained by Schiele from gum benzoin. It is also present in Peru balsam and Tolu balsam in the form of its benzyl ester (benzyl benzoate).



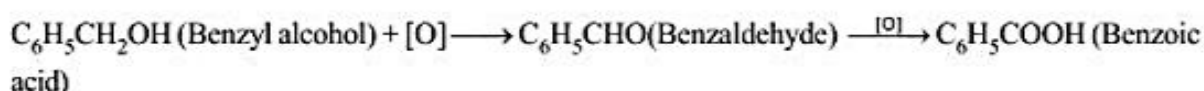
In combined form it is found as benzoylglycine in horse urine.



### (1) Preparation

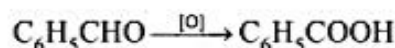
#### (1) Oxidation of Benzyl Alcohol :

Benzoic acid is formed on permanganate oxidation of benzyl alcohol.



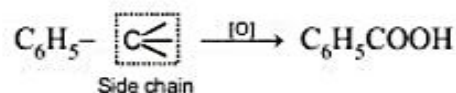
#### (2) Oxidation of Benzaldehyde :

Oxidation of benzaldehyde takes place very readily and benzoic acid is formed.



#### (3) Oxidation of Aralkanes and Their Derivatives :

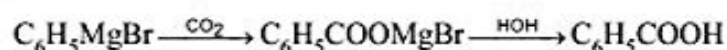
A side chain (alkyl group or substituent alkyl group) bonded directly to the benzene ring is converted to a carboxyl group on oxidation. Dilute nitric acid or chromic acid or alkaline permanganate can be used as oxidant.



Benzoic acid is obtained on oxidation of many compounds like aralkanes (toluene, ethylbenzene, n-propylbenzene, cumene, etc.) and their oxygenated derivatives (benzyl alcohol, benzaldehyde, acetophenone, benzophenone, etc.) halogenated derivatives (benzyl chloride, benzal chloride, benzotrichloride etc) nitrogenated derivatives (cyanobenzene benzamide, etc.)

#### (4) Carboxylation of Grignard's Reagents :

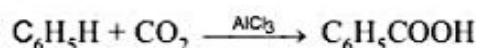
Benzoic acid is formed on hydrolysis of the product obtained by passing carbon dioxide in ethereal solution of phenylmagnesium bromide.



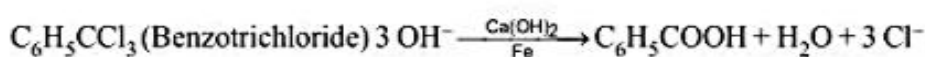


**(5) Carboxylation of Benzene :**

Benzoic acid is obtained on heating benzene and carbon dioxide in nitrobenzene medium in the presence of anhydrous aluminium chloride.

**(6) Alkaline Hydrolysis of Benzotrichloride :**

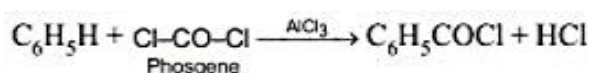
Benzoic acid is formed on hydrolysis of benzotrichloride by lime water in the presence of iron catalyst.

**(7) Hydrolysis of Benzoyl Chloride :**

Benzoic acid is obtained by hydrolysis of benzoyl chloride



Benzoyl chloride is prepared by Friedel–Crafts chlororformylation of benzene, Benzoic acid is obtained in 60% yield by the method.

**(8) Hydrolysis of Cyanobenzene :**

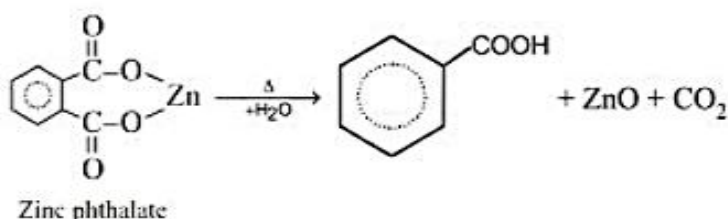
Benzoic acid is formed on hydrolysis of cyanobenzene i.e., benzonitrile by dilute hydrochloric acid.

**(9) Dehydroxylation of Hydroxybenzoic Acid :**

Benzoic acid is formed on dry distillation of o-, m- or p-hydroxybenzoic acid with zinc dust. The ortho isomer is called salicylic acid.

**(10) Decarboxylation of Phthalic Acid :**

o-Benzendicarboxylic acid is called phthalic acid. On heating its zinc or nickel or chromium salt at 200–300° with water vapours, benzoic acid is formed by partial decarboxylation.



**(11) Hydrolysis of Benzoic Acid Derivatives :**

Benzoic acid is formed on hydrolysis of esters, anhydride, acid chloride and amide of benzoic acid.



Benzoyl chloride and benzoic anhydride very readily get hydrolysed by water, but with little bit more difficulty as compared to aliphatic acid chlorides. Hydrolysis by alkali takes place faster.



Hydrolysis of benzoic esters takes place on heating with an alkali.



Hydrolysis of benzamide takes place on boiling with dilute acid or alkali solution.



Liberation of ammonia gas on heating the solution after adding sodium hydroxide solution is the test for amides.

**(2) Physical Properties**

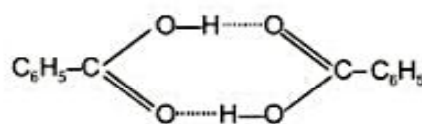
Benzoic acid is a crystalline solid (melting point  $122^\circ$ ) which is sparingly soluble in cold water, but readily soluble in hot water. It is also soluble in organic solvents like alcohol ether, etc. Its acid strength is more than that of the alkanolic acids due to weak negative inductive effect of phenyl group.

**(3) Resonance in Benzoic Acid**

The COOH group present in benzoic acid is a strong electron-attracting group due to which the benzene ring is deactivated and rate of  $\text{S}_\text{E}$  reaction decreases as compared to unsubstituted benzene. Therefore, the COOH group exerts a deactivating effect on the benzene ring.

**Dimerisation in Benzoic Acid due to Hydrogen Bonding :**

Benzoic acid in liquid phase (in benzene solution or in molten form) exists in the form of a dimer by association due to intermolecular hydrogen bonding in the same fashion as in alkanolic acids. This is the reason why the experimental value of the molecular weight of benzoic acid is twice the calculated value.



Hydrogen bonded dimer of benzoic acid

**(4) Reactions**

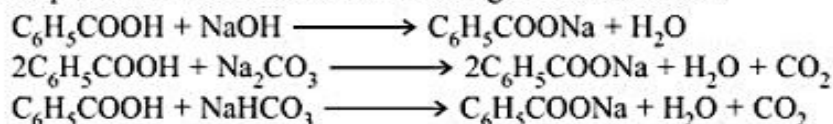
Benzoic acid gives the following two types of reactions.

- (A) Reactions due to COOH group
- (B) Reactions due to  $\text{C}_6\text{H}_5$  group

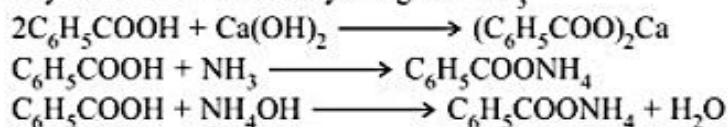
## (A) Reaction Due to Carboxyl Group

### 1. With Bases :

Many alkaline compounds form benzoate salts on reacting with benzoic acid.

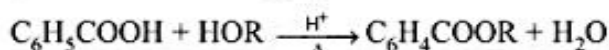


Phenol (a weak acid) does not react with sodium bicarbonate, whereas benzoic acid gives effervescence of  $\text{CO}_2$ , although both are acidic organic compounds toward litmus. Therefore, distinction between phenol and carboxylic acids can be done by using  $\text{NaHCO}_3$ .



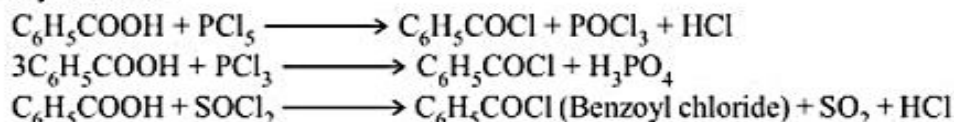
### 2. With Alcohols :

An alkyl benzoate is formed by esterification on heating a mixture benzoic acid and an alkanol in the presence of a few drops of concentrated  $\text{H}_2\text{SO}_4$ .



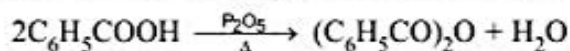
### 3. With Inorganic Chloride :

Benzoyl chloride is formed on the reaction of benzoic acid with phosphorus pentachloride or phosphorus trichloride or thionyl chloride.



### 4. With $\text{P}_2\text{O}_5$ :

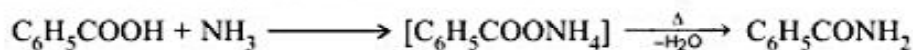
Benzoic anhydride is formed on heating benzoic acid with  $\text{P}_2\text{O}_5$ .



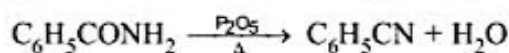
Acetic anhydride also dehydrates two molecules of benzoic acid to give benzoic anhydride.

### 5. With Ammonia :

Benzamide is formed on heating benzoic acid with ammonia.

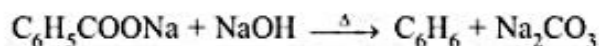


Benzonitrile or cyanobenzene can be obtained by heating benzamide with  $\text{P}_2\text{O}_5$ .



### 6. With Soda Lime :

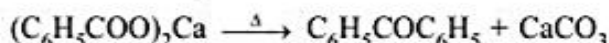
Benzene is obtained on dry distillation of sodium salt of benzoic acid with sodalime.



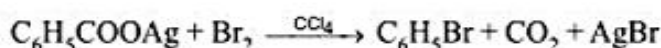


**7. Dry Distillation of Calcium Salt :**

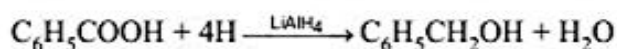
Benzophenone is obtained on dry distillation of calcium salt of benzoic acid.

**8. Hunsdiecker Reaction :**

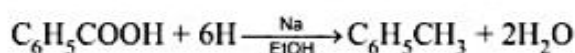
Bromobenzene is formed on heating the silver salt of benzoic acid with bromine in carbon tetrachloride solution

**9. Reduction by Lithium Aluminium Hydride :**

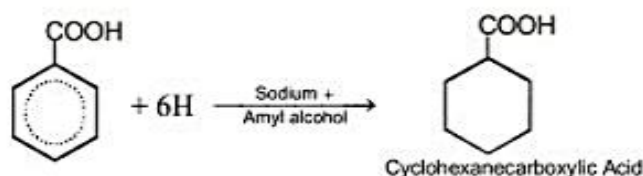
Benzyl alcohol is formed on reduction of benzoic acid by lithium aluminium hydride ( $\text{LiAlH}_4$ ).

**10. Reduction by Sodium and Ethanol :**

Toluene is formed on reduction of benzoic acid by sodium and ethanol.

**(B) Reaction Due to Aromatic Ring****Hydrogenation by Sodium and Amyl Alcohol :**

The  $\text{COOH}$  group is not affected on reduction of benzoic acid by sodium and amyl alcohol but benzene ring of benzoic acid is completely hydrogenated to form Cyclohexanecarboxylic acid.

**Aromatic Electrophilic Substitution Reaction :**

Meta substitution products are formed on halogenation nitration and sulphonation of benzoic acid.





## LIQUID SOLUTIONS

### SOLUTION

A homogeneous mixture of two or more pure substances whose composition may be altered within certain limits is termed as solution.



#### Characteristics of Solution

- (i) It is homogeneous in nature, yet retaining the properties of its constituents.
- (ii) It is made of two parts i.e. a solute and a solvent.



Which component to take as solute and which component to take as solvent depends on physical state of the components.

- (iii) The component which has the same physical state in pure form as the solution is called solvent and the other is called solute. Example, in case of solution of sugar and water, sugar is the solute and water is solvent.
- (iv) If both the components have same state as the solution, the one component which is in excess is called solvent and the other is called solute. Example, alcohol in water, benzene in toluene etc.

#### Types of Solution

S.No.	Solvent	Solute	Examples
1.	Gas	Gas	Mixture of gases, air.
2.	Gas	Liquid	Water vapour in air, mist.
3.	Gas	Solid	Sublimation of a solid into a gas, smoke storms.
4.	Liquid	Gas	CO <sub>2</sub> gas dissolve in water (aerated drink), soda water.
5.	Liquid	Liquid	Mixture of miscible liquids e.g. alcohol in water.
6.	Liquid	Solid	Salt in water, sugar in water.
7.	Solid	Gas	Adsorption of gases over metals, hydrogen over palladium.
8.	Solid	Liquid	Mercury in zinc, mercury in gold i.e. all amalgams.
9.	Solid	Solid	Homogeneous mixture of two or more metals (i.e. alloys) e.g. copper in gold. zinc in copper.



Which of the above types can never have a heterogenous mixture.

## METHODS OF EXPRESSING THE CONCENTRATION OF A SOLUTION

There are many ways of expressing the concentration of a solution. These methods are as follows-



Students should memorise all the formulas and should be comfortable in converting one concentration term to another.



Comment which of the following concentration terms are temperature dependent and which are temperature independent.

### (i) Mass percentage :

It may be defined as the number of parts by mass of solute per hundred parts by mass of solution.



For example, a 5% (by mass) solution of sugar in water means that 100 g of solution contain 5 g of sugar.

$$\text{Mass Percentage} = \frac{\text{Mass of any component}}{\text{total mass}} \times 100$$

### (ii) Volume percentage :

It may be defined as the number of parts by volume of solute per hundred parts by volume of solution.



For example, a 25% (by volume) solution of ethyl alcohol means that 100 cm<sup>3</sup> of the solution contain 25 cm<sup>3</sup> of ethyl alcohol and 75 cm<sup>3</sup> of water.

$$\text{Volume percentage} = \frac{\text{Volume of component}}{\text{total volume of solution}} \times 100$$

### (iii) Mass fraction :

If  $W_A$  is the mass of component A and  $W_B$  the mass of component B in the solution, then the mass fraction of component A and B is written as

$$\text{Mass fraction of A} = \frac{W_A}{W_A + W_B}$$

$$\text{Mass fraction of B} = \frac{W_B}{W_A + W_B}$$

### (iv) Mole fraction

Mole fraction may be defined as the ratio of the number of moles of one component to the total number of moles of all the components (i.e. solute and solvent) present in the solution.

Let us suppose that a solution contains the components A and B and suppose that a gram of A and b gram of B are present in it. Let the molecular masses of A and B be  $M_A$  and  $M_B$  respectively.

Then number of moles of A are given by  $n_A = \frac{a}{M_A}$

and number of moles of B are given by  $n_B = \frac{b}{M_B}$

Total number of moles of A and B =  $n_A + n_B$

Mole fraction of A,  $X_A = \frac{n_A}{n_A + n_B}$

Mole fraction of B,  $X_B = \frac{n_B}{n_A + n_B}$



Sum of mole fractions of all components is always one.

$$\text{i.e. } X_A + X_B = \frac{n_A}{n_A + n_B} + \frac{n_B}{n_A + n_B} = 1$$

So if mole fraction of one component of a binary solution is known say  $X_B$ , then the mole fraction of  $X_A = 1 - X_B$ .



It may be noted that the mole fraction is always independent of the temperature.

#### (v) Mole percent

Mole percent is the number of moles of a component in 100 mole of the solute and solvent.

Mole percent = Mole fraction  $\times 100$

Example. for a solution containing 8 moles  $\text{NH}_3$  and 12 moles of  $\text{H}_2\text{O}$ .

$$\text{Mole fraction of } \text{NH}_3, X_{\text{NH}_3} = \frac{8 \text{ mole}}{12 \text{ moles} + 8 \text{ moles}} = \frac{2}{5}$$

$$\text{Mole percent of } \text{NH}_3 = \frac{2}{5} \times 100 = 40 \text{ mole } \%$$

#### (vi) Parts per million (ppm)

When a solute is present in trace amounts, its concentration is expressed in parts per million. It may be defined as the number of parts by mass of solute per million parts by mass of the solution.



$$\text{Parts per million (ppm)} = \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 10^6$$

#### (vii) Molarity (M)

Molarity of a solution is defined as the number of moles of the solute dissolved per litre of the solution. It is represented by capital M. Mathematically,

$$\text{Molarity (M)} = \frac{\text{Mass of the solution in gram per litre}}{\text{Molecular mass of the solute}}$$

A solution having molarity "one" is called molar solution.



It may be remembered that both normality as well as molarity of a solution changes with change in temperature.



**(viii) Molality (m) -**

Molality of a solution may be defined as the number of moles of the solute dissolved in 1000 gm (1 kg) of the solvent. It is represented by small 'm'. Mathematically

$$\text{Molality (m)} = \frac{\text{Mass of the solute in gram per kg of solvent}}{\text{Molecular mass of the solute}}$$

A solution containing one mole of solute per 1000 gm of solvent (1 kg) has molality equal to one and is called molal solution. Molality is expressed in units of moles per kilogram ( $\text{mol kg}^{-1}$ ).



The molality of a solution does not change with temperature.

**(ix) Normality :**

Normality of a solution is defined as the number of gram equivalent of the solute dissolved per litre of the solution. It is represented by N. Mathematically,

$$\text{Normality N} = \frac{\text{Mass of solute in gram per litre}}{\text{Equivalent mass of the solute}}$$

A solution having normality equal to one is called "normal solution". Such a solution contains one gram equivalent of solute per litre of solution. A seminormal solution contains 0.5 gram equivalent of solute. A decinormal solution contains 0.1 gram equivalent and a centinormal solution contains 0.01 gram equivalent of solute per litre of solution.

$$\text{or Normality} = \frac{\text{Mass of the solution} \times 1000}{\text{Equivalent mass of the solute} \times V}$$

Where V is the volume in milliliter.

**(x) Formality (F) :**

It may be defined as the number of gram formula masses of the ionic solutes dissolved per litre of the solution. Mathematically

$$\text{Formality (F)} = \frac{\text{Mass of the ionic in gram per litre}}{\text{Formula mass of the solute}}$$

Commonly, the term formality is used to express the concentration of the ionic solids which do not exist as molecule but as network of ions.



**Illustration**

1. A storage battery contains a solution of  $\text{H}_2\text{SO}_4$  30% by weight. Find out  
 (i) Molality (ii) Molarity (iii) Normality (iv) Mole fraction of  $\text{H}_2\text{SO}_4$   
 (Given density of solution =  $1.2 \text{ gm/cm}^3$ )

**Sol.** 30% by weight  $\Rightarrow W_{\text{solute}} = 30 \text{ gm}$ ,  $W_{\text{solution}} = 100 \text{ gm}$ ,  $W_{\text{solvent}} = 70 \text{ gm}$

$$V_{\text{solution}} = \frac{100}{1.2} \text{ mL}$$

$$n_{\text{solute}} = \frac{30}{98} = 0.306 \quad n_{\text{solvent}} = \frac{70}{18} = 3.889$$

$$(i) \quad \text{Molality} = \frac{n_{\text{solute}} \times 1000}{W_{\text{solvent}}} = \frac{0.306 \times 1000}{70} = 4.37 \text{ m}$$

$$(ii) \quad \text{Molarity} = \frac{n_{\text{solute}} \times 1000}{V_{\text{solution}}} = \frac{0.306 \times 1000}{\frac{100}{1.2}} = 3.67 \text{ M}$$

$$(iii) \quad \text{Normality} = \frac{W_{\text{solute}} \times 1000}{E_{\text{solute}} \times V_{\text{solution}}} = \frac{30 \times 1000}{49 \times \frac{100}{1.2}} = 7.34 \text{ N}$$

Alternatively

$$\begin{aligned} \text{Normality} &= n\text{-factor} \times \text{Molarity} \\ &= 2 \times 3.67 = 7.34 \end{aligned}$$

$$(iv) \quad x_{\text{H}_2\text{SO}_4} = \frac{n_{\text{H}_2\text{SO}_4}}{n_{\text{H}_2\text{SO}_4} + n_{\text{H}_2\text{O}}} = \frac{0.306}{0.306 + 3.889} = 0.07$$

**Exercise**

1. In a solution mole fraction of solute is 0.2. Find out molality of solution. (Given molar mass of solute  $40 \text{ gm mole}^{-1}$ )

**Ans.** 13.89 m

2. 14.2 gm  $\text{Na}_2\text{SO}_4$  is dissolved in 400 mL water. Find out (i) formality (ii) Normality of solution.

**Ans.** 0.25, 0.75

**SOLUBILITY OF GASES**

We are familiar that gases are completely miscible with each other. Gases also dissolve in liquids and solids. For example, soda-water contains carbon dioxide dissolved in water under high pressure. Oxygen is sufficiently soluble in water to allow survival of aquatic life in lakes, rivers and oceans. An example of dissolution of a gas in a solid is the solubility of hydrogen gas in palladium.

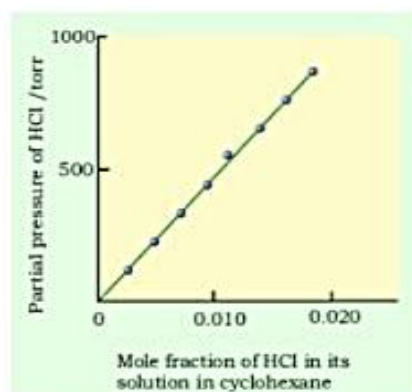
The solubility of a gas in a liquid is determined by several factors. In addition to the nature of the gas and the liquid, solubility of the gas depends on the temperature and pressure of the system. The solubility of a gas in a liquid is governed by Henry's Law which states that the solubility of a gas in a liquid is directly proportional to the pressure of the gas.

Dalton, a contemporary of Henry, also concluded independently that the solubility of a gas in a liquid solution is a function of the partial pressure of the gas. If we use the mole fraction of the gas in the solution as a measure of its solubility, then:



Mole fraction of the gas in a solution is proportional to the partial pressure of the gas. Or, partial pressure of the gas in solution =  $K_H \times$  mole fraction of the gas in solution. Here  $K_H$  is Henry's law constant or  $p = K_H \times$ .

If we draw a graph between partial pressure of the gas versus mole fraction of the gas in solution, then we should get a plot of the type as shown in figure.



**Figure : Experimental results for the solubility of HCl gas in cyclohexane at 293 K. The slope of the line is the Henry's Law constant ( $K_H$ )**



Different gases have different  $K_H$  values at the same temperature. This suggests that  $K_H$  is a function of the nature of the gas.

It is obvious that the higher the value of  $K_H$  at a given pressure, the lower is the solubility of the gas in the liquid. It has been observed that  $K_H$  value for both  $N_2$  and  $O_2$  increases with increase of temperature indicating that solubility of gases decreases with increase of temperature. It is due to this reason that aquatic species are more comfortable in cold waters rather than warm waters.

Henry's law finds several applications in industry and explains some biological phenomena. Notable among these are:

- To increase the solubility of  $CO_2$  in soft drinks and soda water, the bottle is sealed under high pressure.
- To minimize the painful effects accompanying the decompression of deep sea divers, oxygen diluted with less soluble helium gas is used as breathing gas.
- In lungs, where oxygen is present in air with high partial pressure, haemoglobin combines with oxygen to form oxyhaemoglobin. In tissues where partial pressure of oxygen is low, oxyhaemoglobin releases oxygen for utilization in cellular activities.

**Limitations of Henry's Law : For Henry's law to be applicable**

- (i) Gas should not react with solvent.
- (ii) Gas should not associate or dissociate in solution.
- (iii) This law is not applicable for highly concentrated solutions.

**Illustration**

1. If  $N_2$  gas is bubbled through water at 293K, how many millimoles of  $N_2$  gas would dissolve in 1 litre of water. Assume that  $N_2$  exerts a partial pressure of 0.987 bar. Given that Henry's law constant for  $N_2$  at 293 K is 76.48 k bar.

**Sol.** The solubility of gas is related to its mole fraction in the aqueous solution. The mole fraction of the gas in the solution is calculated by applying Henry's law. Thus,

$$x_{N_2} = \frac{p_{N_2}}{K_H} = \frac{0.987 \text{ bar}}{76480 \text{ bar}} = 1.29 \times 10^{-5}$$

As 1 litre water contains 55.5 mol of it, therefore, if  $n$  represents number of moles of  $N_2$  in solution,

$$x_{N_2} = \frac{n \text{ mol}}{n \text{ mol} + 55.5 \text{ mol}} \approx \frac{n}{55.5} = 1.29 \times 10^{-5}$$

Thus,  $n = 1.29 \times 10^{-5} \times 55.5 \text{ mol} = 7.16 \times 10^{-4} \text{ mol}$

$$= 7.16 \times 10^{-4} \text{ mol} \times \frac{1000 \text{ m mol}}{1 \text{ mol}} = 0.716 \text{ m mol}$$

**Exercise**

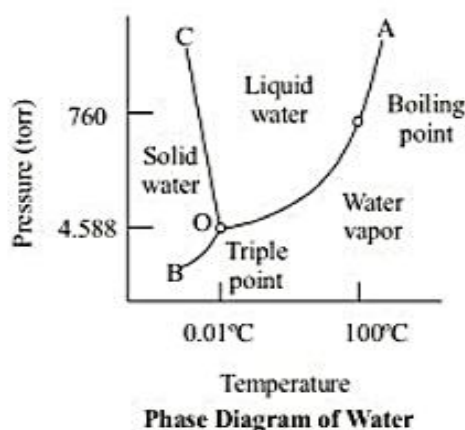
1. Henry's law constant for oxygen and nitrogen dissolved in water at 298K are  $2.0 \times 10^9 \text{ Pa}$  and  $5.0 \times 10^9 \text{ Pa}$ , respectively. A sample of water at a temperature just above 273 K was equilibrated with air (20% oxygen and 80% nitrogen) at 1 atm. The dissolved gas separated from a sample of this water and then dried. Determine the composition of this gas.

**Ans.** Amount percent of  $O_2 = 38.27\%$ , Amount percent of  $N_2 = 61.73\%$

**Phase Diagram of water**

The lines represent simultaneous values of pressure and temperature at which two phases may be present at equilibrium. At the temperatures and pressures that lie on the line OA, liquid water and its vapor are at equilibrium. Along the line OB, ice and its vapor are at equilibrium, while the sets of temperature and pressure at which both ice and liquid water are in equilibrium lie along OC. Only at the pressure and temperature corresponding to the triple point ( $0.01^\circ\text{C}$ , 4.588 torr) are ice, water and water vapor simultaneously present at equilibrium. The areas between the curves represent temperatures and pressures at which only one phase can exist.

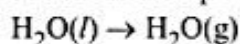




## VAPOUR PRESSURE OF SOLUTION AND RAOULTS LAW

### (i) Vapour Pressure

If a sample of water in its liquid phase is placed in an empty container, some of it will vaporize to form gaseous water. This change is called evaporation. We can write an equation for evaporation occurring spontaneously as if it were as chemical equation :



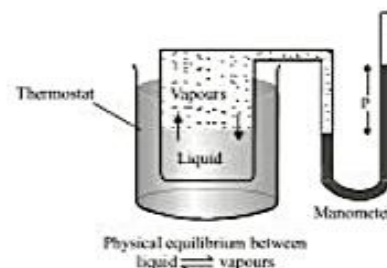
$$K_p = P_{\text{H}_2\text{O}}$$

where

$K_p$  = equilibrium constant

$P_{\text{H}_2\text{O}}$  = vapour pressure of  $\text{H}_2\text{O}(g)$

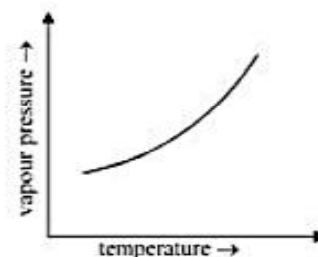
The pressure exerted by the vapour (molecules in the vapour phase) over the surface of the liquid at the equilibrium at given temperature is called the vapour pressure of the liquid.



Is vapour pressure dependent on surface area and shape of the container?

### Factors affecting vapour pressure

**(a) Temperature :** Vapour pressure  $\propto$  Temperature  
The temperature at which the vapour pressure of the liquid becomes equal to the atmospheric pressure is called its **boiling point**.



Can you guess what will be the equation relating vapour pressure and temperature.



**(b) Nature of liquid:**

Vapour pressure of liquid  $\propto \frac{1}{\text{The strength of intermolecular forces acting between molecules}}$

For example,  $\text{CCl}_4$  has higher vapour pressure because of the weak intermolecular forces acting between its molecules than water which has stronger intermolecular forces acting between water molecules of volatile liquid has lower boiling point than a non-volatile liquid.

- (ii) **Raoult's Law for volatile solute :** For a two component solution A (volatile) and B (volatile) the vapour pressure of solution is given by



Vapour pressure of solution = Vapour pressure of solvent in solution + Vapour pressure of solute.

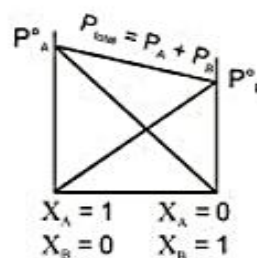
According to Raoult's Law partial pressure of a component is equal to its mole fraction in solution multiplied with partial pressure in pure state

$$\text{Thus } P_A = P_A^\circ X_A$$

$P_A^\circ$  = vapour pressure in pure state of A

$X_A$  = Mole fraction of A in solution

$P_A$  = Partial pressure of A in solution



$$\text{Total vapour pressure of solution } P = P_A^\circ X_A + P_B^\circ X_B$$

**Illustration**

1. At  $25^\circ\text{C}$ , the vapour pressure of methyl alcohol is 96.0 torr. What is the mole fraction of  $\text{CH}_3\text{OH}$  in a solution in which the (partial) vapor pressure of  $\text{CH}_3\text{OH}$  is 23.0 torr at  $25^\circ\text{C}$ ?

**Sol.** 
$$X_{\text{CH}_3\text{OH}} = \frac{P_{\text{CH}_3\text{OH}}}{P_{\text{CH}_3\text{OH}}^\circ} = \frac{23}{96} = 0.24$$

**Exercise**

1. The vapour pressure of ethanol and methanol are 44.5 mm and 88.7 mm Hg respectively. An ideal solution is prepared at the same temperature by mixing 60 g of ethanol with 40 g of methanol. Calculate total vapour pressure of the solution.

**Ans.** 66.13 mm Hg

- (iii) **Relative Lowering of Vapour Pressure :** When a small amount of a **non-volatile solute** is added to the liquid (solvent). It is found that the vapour pressure of the solution is less than that of the pure solvent. This is due to the fact that the solute particles occupy a certain surface area and evaporation takes place from the surface only. The particles of the solvent will have a less tendency to change

into vapour i.e. the vapour pressure of the solution will be less than that of the pure solvent and it is termed as **lowering of vapour pressure**.

For a solution of non-volatile solute with volatile solvent.

$$P = P_A X_A \quad P = \text{vapour pressure of solution}$$

$$P_A = P_A^0 X_A \quad P_A = \text{vapour pressure of solvent}$$

If mole fraction of solute is  $X_B$ , then  $X_A$  = mole fraction of solvent and  $P_A^0$  = vapour pressure of pure solvent.

$$X_A + X_B = 1$$

$$P_A = P_A^0 (1 - X_B) = P_A^0 - P_A^0 X_B$$

$$X_B = \frac{P_A^0 - P_A}{P_A^0}$$



$(P_A^0 - P_A)$  is the **lowering of vapour pressure** whereas  $\left(\frac{P_A^0 - P_A}{P_A^0}\right)$  is called **relative lowering of vapour pressure**.

$$\text{Mole fraction of solute} = \frac{\text{Vapour pressure of pure solvent} - \text{Vapour pressure of solution}}{\text{vapour pressure of solvent}}$$

### Illustration

1. The vapour pressure of pure liquid solvent A is 0.80 atm. When a nonvolatile substance B is added to the solvent its vapour pressure drops to 0.60 atm. What is the mole fraction of component B in the solution?

Ans. 0.25

Sol.  $x_B = \frac{P_A^0 - P_{\text{sol}}}{P_A^0} = \frac{0.80 - 0.60}{0.80} = 0.25$

### Exercise

1. Two liquids A and B form an ideal solution at temperature T. When the total vapour pressure above the solution is 400 torr, the mole fraction of A in the vapour phase is 0.40 and in the liquid phase 0.75. What are the vapour pressure of pure A and pure B at temperature T?

Ans.  $P_A^0 = 213.33$  torr,  $P_B^0 = 960.0$  torr

2. The vapour pressure of pure water at 25°C is 23.76 torr. The vapour pressure of a solution containing 5.40 g of a nonvolatile substance in 90.0 g water is 23.32 torr. Compute the molecular weight of the solute.

Ans. 57.24 g/mol

3. What weight of the non-volatile solute, urea needs to be dissolved in 100 g of water, in order to decrease the vapour pressure of water by 25%? What will be the molality of the solution?

Ans. 111.1g, 18.52 molal



So Raoult's law can also be defined as "For a solution containing non-volatile solute, at a particular temperature. The relative lowering of vapour pressure is equal to mole fraction of the solute".



Vapour pressure of solutions having non volatile solute will always be less than that of solvent, however vapour pressure of solutions with volatile solute may be more or less than that of pure solvent.

#### (iv) Types of Solutions

**(a) Ideal Solution :** An ideal solution may be defined as the one which obeys Raoult's law over all concentration ranges at a given temperature. The total vapour pressure of an ideal solution containing liquids A and B is given by the following equation.

$$P = P_A + P_B = P_A^0 X_A + P_B^0 X_B$$

In an ideal solution of two components A and B, all attractive forces between A and B molecules or between A and A molecules or between B and B molecules (A-B, A-A and B-B) must be identical so that the escaping tendency of an A or B molecule is independent of whether it is surrounded by A molecules, B, molecules or varying proportions of A and B molecules. The escaping tendency of pure liquid A in solution remains the same. Similarly the escaping tendency of B remains the same. Liquids form ideal solution only when they have nearly same molecular size and related constitution so that they have similar molecular environment in the pure state as well as in solution. A perfect ideal solution is rare but many liquids form nearly ideal solution. Liquid heptane and hexane form an ideal solution because the interaction between a hexane molecule and another heptane molecule is the same as the interaction between two heptane molecules other examples of **ideal solutions** are:



benzene + toluene,  
ethyl bromide + ethyl iodide;  
ethyl alcohol + methyl alcohol

chlorobenzene + bromobenzene;  
n-butyl chloride + n-butyl bromide

#### Conditions for forming ideal solution:

Two liquids on mixing form an ideal solution only when

1. both have similar structures and polarity so that they have similar molecular environment.
2. both have similar molecular sizes.
3. both have identical intermolecular forces.

**(b) Non-ideal solutions :** Solutions which do not obey Raoult's law over all concentration ranges at constant temperature are called non-ideal solutions.



### Distinction between ideal & non ideal solutions

S.No.	Ideal solution	Non Ideal solution
1.	They obey Raoult's Law	They do not obey Raoult's Law
2.	$\Delta H_{\text{mixing}} = 0 \Rightarrow$ no heat is absorbed or released during dissolution	$\Delta H_{\text{mixing}} \neq 0 \Rightarrow$ heat is absorbed or released during dissolution
3.	$\Delta V_{\text{mixing}} = 0 \Rightarrow$ the total volume of the solution is equal to the sum of the volume of the pure liquids mixed to form the solution	$\Delta V_{\text{mixing}} \neq 0 \Rightarrow$ the total volume of the solution is not equal to the sum of the volume of the pure liquids mixed to form the solution.
4.	In ideal solution $P_A = P_A^0 X_A$	In non ideal solution $P_A \neq P_A^0 X_A$
5.	Components of ideal solution can be separated in pure form by fractional distillation	Components of non ideal solution can not be separated in pure form by fractional distillation

### Types of non-ideal solutions

- (I) Non ideal solutions showing positive deviation
- (II) Non ideal solutions showing negative deviation.

#### (I) Non ideal solutions showing positive deviation

**Condition for forming non-ideal solution showing positive deviation from Raoult's law.**

Two liquids A and B on mixing form this type of solution when

1. A—B attractive force should be weaker than A—A and B—B attractive forces.
2. 'A' and 'B' have different shape, size and character.
3. 'A' and 'B' escape easily showing higher vapour pressure than the expected value.

#### Example :

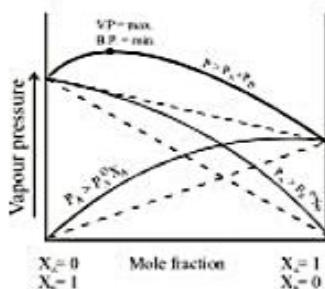


acetone + ethanol;  
water + ethanol;  
acetone + benzene;

acetone +  $\text{CS}_2$   
 $\text{CCl}_4$  + toluene;  
 $\text{CCl}_4$  +  $\text{CH}_3\text{OH}$ ;

water + methanol;  
 $\text{CCl}_4$  +  $\text{CHCl}_3$ ;  
cyclohexane + ethanol

### Graphical representation of vapour pressure of non-ideal solution showing positive deviation





## (II) Non ideal solutions showing negative deviation.

Condition for forming non-ideal solution showing negative deviation from Raoult's law.

Two liquids A and B on mixing form this type of solution when

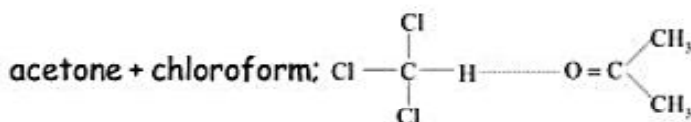
1. A—B attractive force should be greater than A—A and B—B attractive forces.
2. 'A' and 'B' have different shape, size and character
3. Escaping tendency of both components 'A' and 'B' is lowered showing lower vapour pressure than expected ideally.

Example:

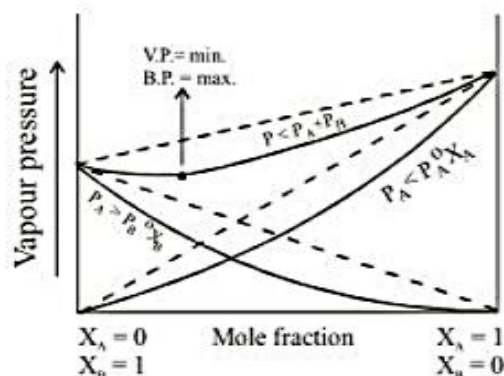


acetone + aniline;  
chloroform + diethyl ether,  
chloroform + benzene  
water + HCl

$\text{CH}_3\text{OH} + \text{CH}_3\text{COOH}$ ;  
acetic acid + pyridine;  
 $\text{H}_2\text{O} + \text{HNO}_3$ ;



Graphical representation of vapour of non-ideal solution showing negative deviation



Distinction between non ideal solutions showing positive deviation & negative deviation

S.No.	Showing positive deviation	Showing negative deviation
1.	$\Delta H_{\text{mix}} > 0$ . (endothermic dissolution i.e. heat is absorbed.)	$\Delta H_{\text{mix}} < 0$ . (Exothermic dissolution i.e. heat is evolved.)
2.	$\Delta V_{\text{mix}} > 0$ . (Volume is increased after dissolution)	$\Delta V_{\text{mix}} < 0$ . (Volume is decreased during dissolution)
3.	$p_A > p_A^0 X_A$ ; $p_B > p_B^0 X_B$ , $\therefore p_A + p_B > p_A^0 X_A + p_B^0 X_B$	$p_A < p_A^0 X_A$ ; $p_B < p_B^0 X_B$ , $\therefore p_A + p_B < p_A^0 X_A + p_B^0 X_B$

### (v) Azeotropes



The non-ideal solution showing large deviations from Raoult's law can not be purified by distillation. A solution at certain composition which continues to boil at constant temperature without change in the composition of the solution.

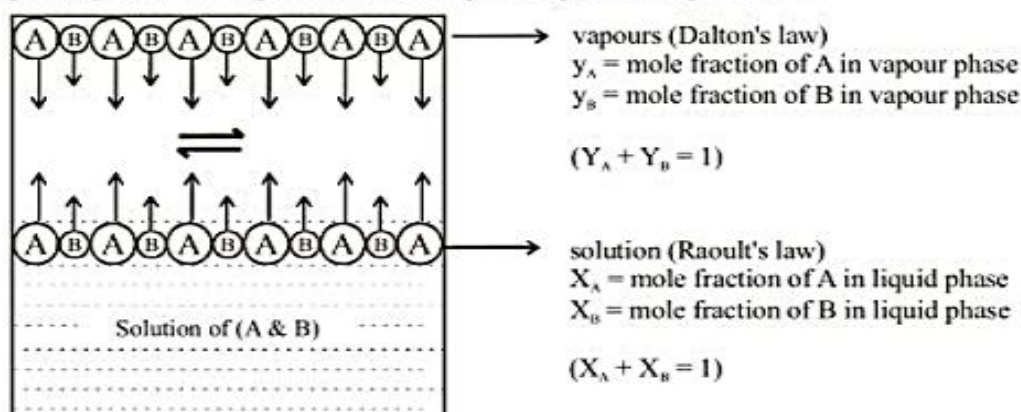
This mixture is called **Azeotrope** or **Constant boiling mixture**. Azeotropes are of two types:

- (a) **Azeotropes with Maximum vapour pressure and Minimum Boiling point :** When liquid in a solution do not have great chemical affinity for each other (+ve deviation from ideality) their higher escape tendencies increase the vapour pressure much more than expected on the basis of Raoult's law. In many cases, the deviations are so extreme as to lead to a maximum in the curve. The point of maximum vapour pressure means that the boiling point at this composition will be minimum and constant.
- (b) **Azeotropes with Minimum vapour pressure and Maximum Boiling Point :** When liquids in solution show -ve deviation from ideality, their escape tendencies and hence the vapour pressure decreases than expected on the basis of Raoult's law. In many cases, the maximum in the temperature composition curve is obtained. The point of minimum vapour pressure in the curve means that the boiling point of this composition will be maximum and constant.

(vi) **Determination of composition in vapour phase**

**Dalton's Law v/s Raoult's Law:**

The composition of the vapour in equilibrium with the solution can be calculated applying Daltons' law of partial pressures. Let the mole fractions of vapours A and B be  $Y_A$  and  $Y_B$  respectively. Let  $p_A$  and  $p_B$  be the partial pressure of vapours A and B respectively and total pressure  $P$ .



From Raoult's law  $P = P_A^0 X_A + P_B^0 X_B$   
 $P_A = P_A^0 X_A$  and  $P_B = P_B^0 X_B$

From Dalton's law,

Partial pressure = Mole fraction  $\times$  Total pressure

For A  $P_A = y_A \times P = P_A^0 X_A$

$$\Rightarrow y_A = \frac{P_A^0 X_A}{P} \quad \text{.....(1)}$$

Similarly

$$\Rightarrow y_B = \frac{P_B^0 X_B}{P} \quad \text{.....(2)}$$

Above formula is used for calculation of mole fraction of B in vapour phase

$$\text{on adding} \quad X_A + X_B = \frac{P \times y_A}{P_A^0} + \frac{P \times y_B}{P_B^0} = 1$$

$$\Rightarrow \frac{1}{P} = \frac{y_A}{P_A^0} + \frac{y_B}{P_B^0} \quad \text{.....(3)}$$

Above formula is used to calculate total vapour pressure when mole fractions are given in vapour phase



$P = P_A^\circ X_A + P_B^\circ X_B \Rightarrow$  This formula is used to calculate total pressure when mole fraction are given in liquid phase

$\frac{1}{P} = \frac{y_A}{P_A^\circ} + \frac{y_B}{P_B^\circ} \Rightarrow$  This formula is used to calculate total pressure when mole fraction are given in vapour phase



Thus, in case of ideal solution the vapour phase is phase is richer with more volatile component i.e., the one having relatively greater vapour pressure.

### Illustration

- The vapour pressures of ethanol and methanol are 44.5 mm and 88.7 mm Hg respectively. An ideal solution is formed at the same temperature by mixing 60 g of ethanol with 40 g of methanol. Calculate the total vapour pressure of the solution and the mole fraction of methanol in the vapour.

**Sol.** No. of moles of  $C_2H_5OH = \frac{60}{46} = 1.304$ , No. of moles of  $CH_3OH = \frac{40}{32} = 1.25$

$$'X_A' \text{ of ethyl alcohol} = \frac{1.304}{1.304 + 1.25} = 0.5107$$

$$'X_B' \text{ of methyl alcohol} = \frac{1.25}{1.304 + 1.25} = 0.4893$$

$$\text{Partial pressure of ethyl alcohol} = X_A \cdot P_A^\circ = 0.5107 \times 44.5 = 22.73 \text{ mm Hg}$$

$$\text{Partial pressure of methyl alcohol} = X_B \cdot P_B^\circ = 0.4893 \times 88.7 = 43.40 \text{ mm Hg}$$

$$\text{Total vapour pressure of solution} = 22.73 + 43.40 = 66.13 \text{ mm Hg}$$

$$\text{Mole fraction of methyl alcohol in the vapour} = \frac{\text{Partial pressure of } CH_3OH}{\text{Total vapour pressure}} = \frac{43.40}{66.13} = 0.6563$$

### Exercise

- At  $90^\circ\text{C}$ , the vapour pressure of toluene is 400 torr and that of  $\sigma$ -xylene is 150 torr. What is the composition of the liquid mixture that boils at  $90^\circ\text{C}$ , when the pressure is 0.50 atm? What is the composition of vapour produced?

**Ans.** 92 mol% toluene; 96.8 mol % toluene

- For an ideal binary liquid solution with  $P_A^\circ > P_B^\circ$ , which relation between  $X_A$  (mole fraction of A in liquid phase) and  $Y_A$  (mole fraction of A in vapour phase) is correct?

(A)  $Y_A < Y_B$       (B)  $X_A > X_B$       (C)  $\frac{Y_A}{Y_B} > \frac{X_A}{X_B}$       (D)  $\frac{Y_A}{Y_B} < \frac{X_A}{X_B}$

**Ans.** (C)



## COLLIGATIVE PROPERTIES



The properties of dilute solutions containing nonvolatile solute, which depends upon relative number of solute and solvent particles but do not depend upon their nature are called colligative properties.

Some of the colligative properties are

- (i) Relative lowering of vapour pressure
- (ii) Elevation in boiling point
- (iii) Depression in freezing point; and
- (iv) Osmotic pressure.

**Factors that Affect the Colligative Property :** The number of solute particles in solution. To be more accurate, the colligative property depends upon the fraction of solute and solvent particles in solution.

- (1) Nature of the solvent
- (2) Independent of the nature of the solute
- (3) Extent of association and dissociation of solute particles in solution.

### (i) Relative Lowering of Vapour Pressure

As shown earlier the mathematical expression for relative lowering of vapour pressure is as follows

$$\frac{\Delta P}{P_A^0} = X_B = \text{mole fraction of solute}$$

$$\Delta P = P_A^0 - P_A = \text{lowering of vapour pressure}$$

$P_A$  = vapour pressure of pure solvent

Molecular mass of non-volatile substance can be determined from relative lowering of vapour pressure

$$\frac{P_A^0 - P}{P_A^0} = \frac{W_B / M_B}{W_A / M_A + W_B / M_B}$$

For dilute solution  $W_B / M_B < W_A / M_A$  and hence  $W_B / M_B$  may be neglected in the denominator. So

$$\frac{P_A^0 - P_A}{P_A^0} = \frac{W_B / M_B}{W_A / M_A} = \frac{W_B}{W_A} \times \frac{M_A}{M_B} \text{ or } M_B = \frac{W_B / M_A}{\left( \frac{P_A^0 - P_A}{P_A^0} \right)}$$

### Illustration

1. One mole of a non-volatile solute is dissolved in two moles of water. The vapour pressure of the solution relative to that of water is

(1)  $2/3$

(2)  $1/3$

(3)  $1/2$

(4)  $3/2$

Sol.  $\frac{P_{\text{solvent}}^0 - P_{\text{solution}}}{P_{\text{solvent}}^0} = \frac{1}{1+2} = \frac{1}{3}$  (mole fraction of solute in solution) Or  $\frac{P_{\text{solution}}}{P_{\text{solvent}}^0} = 1 - \frac{1}{3} = \frac{2}{3}$



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**Exercise**


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1. The vapour pressure of water is 17.54 mm Hg at 293 K. Calculate vapour pressure of 0.5 molal solution of a solute in it.

Ans. 17.38

2. Pressure over ideal binary liquid mixture containing 10 moles each of liquid A and B is gradually decreased isothermally. If  $P_A^\circ = 200$  mm Hg and  $P_B^\circ = 100$  mm Hg, find the pressure at which half of the liquid is converted into vapour.

(A) 150 mm Hg      (B) 166.5 mm Hg      (C) 133 mm Hg      (D) 141.4 mm Hg

Ans. (D)

---

**(ii) Elevation in Boiling Point**

The boiling points elevates when a non-volatile solute is added to a volatile solvent. Which occurs due to lowering of vapour pressure.

The boiling point of a liquid may be defined as **the temperature at which its vapour pressure becomes equal to atmospheric pressure.**

So when a non-volatile solute is added to a volatile solvent results lowering of vapour pressure and consequent elevation of boiling point

where

$$\Delta T_b = T_b - T_b^\circ$$

$\Delta T_b$  = elevation in B.P.

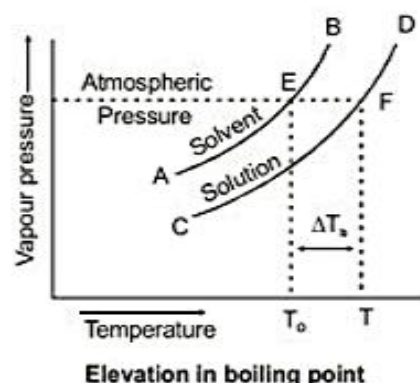
$\Delta P$  = lowering of V.P.

$X_B$  = mole fraction of solute

$K$  = elevation constant

$T_b^\circ$  = boiling point of solvent

$T_b$  = boiling point of solution



It is found that elevation of boiling point is directly proportional to the number of moles of the solute in given amount of the solvent(m).

$$\Delta T_b \propto m$$

$$\Delta T_b \propto K_b m$$

Where 'm' is the molality of solution.

Where  $K_b$  is ebullioscopic or boiling point elevation constant. When molality of the solution is equal to one. Then

$$\Delta T_b = K_b$$

Hence molal elevation constant of the solvent may be defined as the elevation in its boiling point when one mole of non-volatile solute is dissolved per kg (1000 gm) of solvent. The unit of  $K_b$  are  $K \text{ kg mol}^{-1}$ .

Because molality of solution  $m = \frac{W_B}{M_B} \cdot \frac{1000}{W_A}$

---

$$\text{So } \Delta T_b = K_b \frac{W_B}{M_B} \cdot \frac{1000}{W_A}$$

$$M_B = \frac{1000 \times K_b \times W_B}{\Delta T_b \times W_A}$$

Where  $W_A$  = mass of solvent,

$W_B$  = mass of solute,

$M_A$  = Molar mass of solvent,  $M_B$  = Molar mass of solute.

### Determination of $K_b$ of solvent :



$$K_b = \frac{RT_b^2}{1000L_v}$$

.....(3)

where  $R$  is molar gas constant,  $T_b$  is the boiling point of the solvent on Kelvin scale and  $L_v$  the latent heat of vaporization of solvent in calories per gram.

$$\text{For water } K_b = \frac{2 \times (373)^2}{1000 \times 540} = 0.515 \text{ K}\cdot\text{kg/mol}$$



If energy is taken in joule then use  $R = 8.314 \text{ J K}^{-1} \text{ mole}^{-1}$

Energy is taken in calorie then use  $R = 2 \text{ cal K}^{-1} \text{ mole}^{-1}$

### Illustration

1. An aqueous solution of glucose boils at  $100.01^\circ\text{C}$ . The molal elevation constant for water is  $0.5 \text{ K mol}^{-1} \text{ Kg}$ . The number of molecules of glucose in the solution containing 100 g of water is  
(A)  $6.023 \times 10^{23}$  (B)  $6.023 \times 10^{22}$  (C)  $12.046 \times 10^{20}$  (D)  $12.046 \times 10^{23}$

Ans. (C)

$$\text{Sol. } \Delta T_b = K_b \cdot m \quad \text{Or} \quad m = \frac{\Delta T_b}{K_b} = \frac{0.01}{0.5} = .02 \text{ mole Kg}^{-1} \text{ of water}$$

So, the number of moles of glucose in 100 g of water

$$= \frac{0.02 \times 100}{1000} = 0.002 \text{ moles of glucose} \quad = 0.002 \times 6.023 \times 10^{23} = 2 \times 6.023 \times 10^{20}$$

### Exercise

1. Estimate the boiling point of a solution of 25.0g of urea  $\text{NH}_2\text{CONH}_2$  plus 25.0g of thiourea  $\text{NH}_2\text{CSNH}_2$  in 500g of chloroform,  $\text{CHCl}_3$ . The boiling point of pure chloroform is  $61.2^\circ\text{C}$ ,  $K_b$  of chloroform =  $3.63 \text{ K m}^{-1}$ .

Ans.  $66.645^\circ\text{C}$

2. Calculate the molal elevation constant,  $K_b$  for water and the boiling point of 0.1 molal urea solution. Latent heat of vaporisation of water is  $9.72 \text{ kcal mol}^{-1}$  at  $373.15 \text{ K}$ .

Ans.  $K_b = 0.512 \text{ kg mol K}^{-1}$ ,  $T_b = 373.20 \text{ K}$

**(iii) Depression in Freezing Point**

The freezing point of a pure liquid is fixed. If a non-volatile solute is dissolved in a liquid the freezing point of the solution is lowered. The freezing point is that temperature at which the solvent has the same vapour pressure in two phases liquid solution and solid solvent. Since the solvent vapour pressure in solution is depressed. Its vapour pressure will become equal to that of the solid solvent at a lower temperature

$$\Delta T_f = T_f^\circ - T_f$$

It is found that depression in freezing point is directly proportional to the number of moles of the solute in given amount of the solvent(m).

Hence 
$$\Delta T_f \propto m$$
  

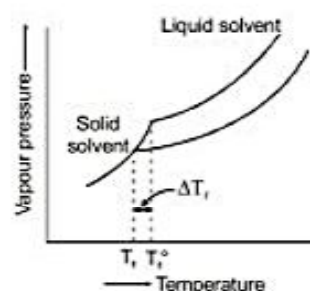
$$\Delta T_f = K_f m$$

Where m = molality of the solution.

$K_f$  = molal depression constant

When molarity (m) of the solution is one, then

$$\Delta T_f = K_f$$



Hence molal depression constant or molal cryoscopic constant may be defined as “the depression in freezing point when one mole of non-volatile solute is dissolved per kilogram (1000 gm) of solvent” and molar depression constant is defined as “the depression in freezing point when one mole of non-volatile solute is dissolved per litre (1000 ml) of solvent.”

The molecular mass of the non-volatile solute may be calculated by the use of following mathematical equation

$$M_B = \frac{K_f \times W_B \times 1000}{W_A \times \Delta T_f}$$

Where  $W_A$  = mass of solvent,  $W_B$  = mass of solute,

$M_A$  = Molar mass of solvent,  $M_B$  = Molar mass of solute.

**Determination of  $K_f$  of solvent**

$K_f$  is characteristic of a particular solvent and can be calculated from the thermodynamical relationship.



$$K_f = \frac{RT_f^2}{1000L_f} \quad \text{.....(3)}$$

where  $T_f$  is the freezing point of solvent in absolute scale and  $L_f$  the latent heat of fusion in calories per gram of the solvent. For water,

$$K_f = \frac{0.002 \times (273)^2}{80} = 1.86 \text{ K}\cdot\text{kg/mole}$$



If energy is taken in joule then use  $R = 8.314 \text{ JK}^{-1} \text{ mole}^{-1}$

Energy is taken in calorie then use  $R = 2 \text{ cal K}^{-1} \text{ mole}^{-1}$



### $K_b$ , $K_f$ for various Solvents

Solvent	B.P.	$K_b$	F.P.	$K_f$
Acetic acid	118.1°C	2.93	17°C	3.9
Benzene	80.2°C	2.53	5.4°C	5.13
Water	100°C	0.53	0°C	1.86

#### Antifreeze solutions -



Water is used in radiators of vehicles as cooling liquid. If the vehicle is to be used at high altitudes where temperature is sub-zero, water would freeze in radiators. To avoid this problem, a solution of ethylene glycol in water is used in radiators which will lower the freezing point lower than zero.

#### Illustration

1. What is the percent by mass of iodine needed to reduce the freezing point of benzene to 3.5°C? The freezing point and cryoscopic constant of pure benzene are 5.5°C and 5.12 K/m respectively.

Sol.  $\Delta T_f = T_f^0 - T_f = K_f \cdot m$   
 $5.5^\circ\text{C} - 3.5^\circ\text{C} = 5.12 \times m$

$$m = \frac{2}{5.12} = 0.39 \text{ molal}$$

$$\therefore \text{Mass of iodine needed for 1000g of benzene} = m \times \text{molecular mass of iodine } I_2$$

$$= 0.39 \text{ mol/kg} \times 254 \text{ g/mol} = 99.06 \text{ g/kg}$$

$$\therefore 1000\text{g} + 99.06\text{g solution contains } 99.06\text{g } I_2$$

$$100\text{g solution contains } \frac{99.06\text{g} \times 100}{1099.06\text{g}} = 9.01\%$$

#### Exercise

1. The elements X and Y form compounds having molecular formula  $XY_2$  and  $XY_4$ . When dissolved in 20 gm of benzene, 1 gm  $XY_2$  lowers the freezing point by 2.3°, whereas 1 gm of  $XY_4$  lowers the freezing point by 1.3°C. The molal depression constant for benzene is 5.1. Calculate the atomic masses of X and Y.

Ans.  $x = 25.6$ ,  $y = 42.6$

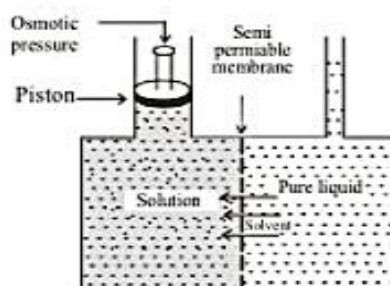
2. Calculate the amount of ice that will separate out of cooling a solution containing 50g of ethylene glycol in 200 g water to -9.3°C. ( $K_f$  for water = 1.86 K mol<sup>-1</sup> kg)

Ans. 38.71 g

#### (iv) Osmotic Pressure

(a) **Osmosis** : Spontaneous flow of solvent molecules through a semipermeable membrane from a pure solvent to the solution (or from a dilute solution to a concentrated solution) is termed as osmosis.





### (b) Osmotic Pressure :

When a solution is separated from the pure solvent with the help of a semipermeable membrane. There occurs the flow of solvent molecules from the pure solvent to the solution side. The flow of solvent molecules from a region of higher concentration of solvent to the region of lower concentration of solvent is termed as the phenomenon of osmosis. This also happens when two solution of different concentrations are separated by a semipermeable membrane.

As a result of osmosis a pressure is developed which is termed as osmotic pressure. It is defined in various methods.

- (1) The excess hydrostatic pressure which builds up as a result of osmosis is called osmotic pressure.
- (2) The excess pressure that must be applied to the solution side to prevent the passage of solvent into it through a semipermeable membrane.
- (3) Osmotic pressure of a solution is equal to the negative pressure which must be applied to the solvent in order to just stop the osmosis.
- (4) The osmotic pressure of a solution may be defined as the extra pressure which should be applied to the solution to increase the 'chemical potential of solvent in solution equal to the chemical potential of the pure solvent at the same temperature.

**(c) Theory of Dilute Solutions :** The osmotic pressure of a dilute solution was the same as the solute would have exerted if it were a gas at the same temperature as of the solution and occupied a volume equal to that of the solution. This generalization is known as **Van't Hoff theory of dilute solutions**. The osmotic pressure is a colligative property. So the osmotic pressure is related to the number of moles of the solute by the following relation

$$\pi V = nRT$$

$$\pi = \frac{n}{V} RT \quad \left( \because \frac{n}{V} = C \right)$$

$$\pi = CRT$$

Here C = concentration of solution in moles per litre;

R = solution constant;

T = temperature in Kelvin degree;

n = number of moles of solute; and

V = volume of solution.

This equation is called **Van't Hoff's equation**.

**(d) Determination of molecular mass from osmotic pressure :** The molecular mass of a substance i.e. solute can be calculated by applying the following formula

$$M = \frac{WRT}{\pi V}$$

Accurate molecular mass will only be obtained under following conditions

- (i) The solute must be non-volatile;
- (ii) The solution must be dilute; and
- (iii) The solute should not undergo dissociation or association in the solution.

**Solution constant R** - The solution constant R has the same significance and value as the gas constant. i.e.

$$\begin{aligned} R &= 0.0821 \text{ litre-atm K}^{-1} \text{ mol}^{-1} \\ &= 8.314 \times 10^{-7} \text{ erg K}^{-1} \text{ mol}^{-1} \\ &= 8.314 \text{ JK}^{-1} \text{ mol}^{-1} \\ &= 8.314 \text{ Nm K}^{-1} \text{ mol}^{-1} \end{aligned}$$

**(e) Type of solutions :**



**(I) Isotonic solution :** The two solutions having equal osmotic pressure are termed as isotonic solution.

**(II) Hypertonic solution :** A solution having higher osmotic pressure than some other solution is said to be called hypertonic solution.

**(III) Hypotonic solution :** A solution having a lower osmotic pressure relative to some other solution is called hypotonic solution.

**(f) Semipermeable membrane :**

A membrane which allows the passage of solvent molecules but not that of solute. When a solution is separated from the solvent by it is known as semipermeable membrane.

Some example of it are as follows

- (a) Copper ferrocyanide  $\text{Cu}_2[\text{Fe}(\text{CN})_6]$ ;
- (b) Calcium phosphate membrane; and
- (c) Phenol saturated with water.

**(g) Reverse Osmosis :**

If a pressure greater than the osmotic pressure is applied on the concentrated solution, the solvent starts to flow from concentrated solution to dilute solution (or pure solvent). This is reverse osmosis. One of its chief uses is desalination of sea water to get pure drinking water.

**Illustration**

1. The solute 'A' is a ternary electrolyte and solute 'B' is a non-electrolyte. If 0.1 M solution of solute 'B' produces an osmotic pressure of 2P, then 0.05 M solution of A at the same temperature will produce an osmotic pressure equal to

(A) P (B) 1.5 P (C) 2 P (D) 3 P

**Ans.** (D)

**Sol.** For ternary electrolyte, osmotic pressure =  $(0.05 \times 3) (R) (T)$

$$\text{Osmotic pressure of B} = 2P = (0.1) (R) (T) \text{ or } P = \frac{0.1}{2} RT$$

$$P = 0.05 RT$$

Since temperature is the same, comparing the two equations, we obtain  
the osmotic pressure of ternary electrolyte = 3P

2. The osmotic pressure of blood is 7.65 atm. at 310 K. An aqueous solution of glucose which is isotonic with blood has the percentage (wt./volume)

(A) 5.41 (B) 3.54 (C) 4.53 (D) 53.4

**Ans.** (A)

**Sol.** Since glucose and blood are isotonic, the osmotic pressures are the same. Therefore,

$$\pi_{\text{glucose}} = \pi_{\text{blood}}$$

$$\text{Or } 7.65 \times V = \frac{w}{180} \times 0.0821 \times 310 \quad [w = \text{amount of glucose present in } V \text{ litres of solution}]$$

$$\text{Or } 7.65 \times 180 = \frac{w}{V} \times 0.0821 \times 310$$

$$\text{Or } \frac{w}{V} = \frac{7.65 \times 180}{0.0821 \times 310} = 54.1 \text{ g L}^{-1} \text{ or } 5.41\%$$

**Exercise**

1. A 250 mL water solution containing 48.0 g of sucrose,  $C_{12}H_{22}O_{11}$ , at 300 K is separated from pure water by means of a semipermeable membrane. What pressure must be applied above the solution in order to just prevent osmosis?

**Ans.** 13.8 atm

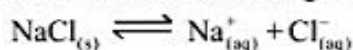
2. A 5% solution (w/v) of cane-sugar (Mol. weight = 342) is isotonic with 0.877% (w/v) of urea solution. Find molecular weight of urea.

**Ans.** 59.99

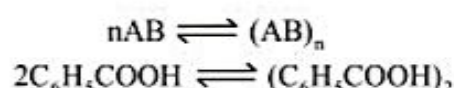


## ABNORMAL MOLECULAR MASSES

Vapour pressure lowering, boiling point elevation, freezing point depression and osmotic pressure are colligative properties which depend upon the fraction of solute and solvent particles in solution and not upon the chemical nature of the solute. If solute molecules dissociates in solution, there are more particles in solution and therefore, lowering of vapour pressure shows an increased effect.



If the solute molecules associates in solution, there are less particles in solution, and therefore lowering of vapour pressure shows a decreased effect.

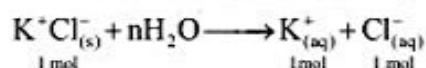


### The molecular mass of a solute is inversely proportional to its molality :

If colligative molality is 2 m, the calculated molecular mass is one-half of the actual molecular mass of the solute. If colligative molality is 3 m, the calculated molecular mass is one third of the actual molecular mass of the solute. The molecular mass of benzoic acid is 122 g/mol. But the molecular mass of benzoic acid dissolved in benzene is found to be 244 g/mol by using a colligative property. Benzoic acid associates to form a dimer and therefore its colligative molality is one-half of the molality of benzoic acid. As molecular mass of a solute is inversely proportional to molality, the molecular mass of benzoic acid determined using a colligative property is double the actual molecular mass of benzoic acid. We can summarize the results as:

#### (i) The extent of dissociation and colligative property :

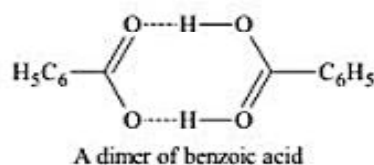
A solute dissociates completely or partially in solution makes available more particles than would otherwise be present in solution and therefore, a colligative property shows an increased effect. For example, molecular masses obtained of strong acids, bases and salts are much less than their normal values. As an example, one particle of potassium chloride on dissociation in water gives two particles,  $\text{K}^{+}$  and  $\text{Cl}^{-}$  and therefore, the molecular mass obtained by a colligative property is half of its normal molecular mass.



#### (ii) The extent of association and colligative property:

A solute that associates in solution provides less particles that would otherwise be present in solution and therefore, the colligative property shows the decreased effect. For example, benzoic acid in benzene is found to have molecular mass which is just twice its normal molecular mass.

It is found that compounds which are capable of forming hydrogen bonds, e.g., phenols, carboxylic acids, alcohols: because of association show decreased effect of colligative property.





## VAN'T HOFF FACTOR

In 1886, Van't Hoff, Jacobus Henricus (Dutch chemist, 1859,-1911) introduced a factor 'i' known as Van't Hoff factor to express the extent to association or dissociation of a solute in solution. It can be calculated as:

$$i = \frac{\text{number of solute particles actually present in solution}}{\text{number of solute particles dissolved}}$$

$$= \frac{\text{Observed colligative property}}{\text{normal colligative property}} = \frac{\text{observed molality}}{\text{normal molality}} = \frac{\text{normal molecular weight of solute}}{\text{observed molecular weight of solute}}$$

The Van't Hoff factor for a solute can be calculated by the following modified equations:

$$(i) \quad \frac{P_A^0 - P_A}{P_A^0} = i X_B \quad (ii) \quad \Delta T_f = i K_f m \quad (iii) \quad \Delta T_b = i K_b m \quad (iv) \quad \pi = i CRT$$

where C is molarity of the solution.

**Note:** For non-electrolytes;  $i = 1$

For electrolytes;  $i > 1$  (If solute particles undergo Dissociation in the solution)

$i < 1$  (If solute particles undergo Association in the solution)

### (iii) Application of Van't Hoff Factor :

#### (a) Calculation of Degree of Dissociation of solute particles:

	$A_n \rightleftharpoons nA$
No. of moles dissolved	1 mol      0
No. of moles after dissociation	$1 - \alpha$ $n\alpha$
Total number of moles present in solution	$= (1 - \alpha) + n\alpha$

$$\text{Van't Hoff factor, } i = \frac{\text{Moles of solute actually present in solution}}{\text{Moles of solute dissolved}}$$

$$= \frac{(1 - \alpha) + n\alpha}{1} = 1 + (n - 1)\alpha \quad \text{or} \quad \alpha = \frac{i - 1}{n - 1}$$

#### (b) Calculation of Degree of Association of solute particles:

Let n moles of the solute, A, associate to form  $(A)_n$ . If  $\alpha$  is the degree of association.

	$nA \rightleftharpoons A_n$
No. of moles dissolved	1 mol      0
No. of moles after dissociation	$1 - \alpha$ $\alpha/n$
Total number of moles present in solution	$= (1 - \alpha) + \alpha/n$

$$i = \left[ 1 - \alpha \left( 1 - \frac{1}{n} \right) \right] \quad \text{Hence} \quad \alpha = \frac{i - 1}{1 - \frac{1}{n}} = (i - 1) \times \frac{n}{1 - n}$$

**Illustration**

1. Molal elevation constant  $K_b$  for water is 0.52 K/m. 0.1 molal solution of NaCl will boil at  
 (A) 100.52°C (B) 100.052°C (C) 101.04°C (D) 100.104°C

Ans. (D)

Sol. If vant Hoff factor is  $i$ , then

$$\Delta T_b = i K_b \cdot m \text{ (for NaCl } i = 2) \\ = 2 \times 0.52 \times 0.1 = 0.104.$$

And, so the boiling point of solution will be 100.104°C.

2. A solution is prepared by dissolving 26.3g of  $\text{CdSO}_4$  in 1000g water. The depression in freezing point of solution was found to be 0.284K. Calculate the Van't Hoff factor. The cryoscopic constant of water is 1.86K kg solvent  $\text{mol}^{-1}$ - solute.

Ans. 1.21

Sol. Molecular mass  $\text{CdSO}_4 = 112.4 + 32 + 4 \times 16 = 208.4 \text{ g/mol}$

$$\text{Molality } \text{CdSO}_4 = \frac{\text{Mass } \text{CdSO}_4}{\text{Molecular mass } \text{CdSO}_4 \times \text{Mass solvent in kg}}$$

$$= \frac{26.3\text{g}}{(208.4\text{g/mol}) \times \left(\frac{1000}{1000} \text{ kg}\right)} = 0.216\text{m}$$

$$\Delta T_f = i K_f \cdot m \text{ or } i = \frac{\Delta T_f}{K_f \cdot m} = \frac{0.284\text{K}}{1.86\text{K/m} \times 0.126\text{m}} = 1.21$$

**Exercise**

1. A decimolar solution of potassium ferrocyanide is 50% dissociated at 300K. Calculate the osmotic pressure of the solution. ( $R=8.314 \text{ JK}^{-1} \text{ mol}^{-1}$ )

Ans.  $7.482 \times 10^5 \text{ Nm}^{-2}$

2. A 1.2% solution (w/v) of NaCl is isotonic with 7.2% solution (w/v) of glucose. Calculate degree of ionization and Van't Hoff factor of NaCl.

Ans. 0.95; 1.95

3. A 0.001 molal solution of a complex  $[\text{MA}_x]$  in water has the freezing point of  $-0.0054^\circ\text{C}$ . Assuming 100% ionization of the complex salt and  $K_f$  for  $\text{H}_2\text{O} = 1.86 \text{ k.m}^{-1}$ , write the correct representation for the complex.

(A)  $[\text{MA}_8]$  (B)  $[\text{MA}_7]\text{A}$  (C\*)  $[\text{MA}_6]\text{A}_2$  (D)  $[\text{MA}_5]\text{A}_3$

Ans. (C)

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**THE ATLAS****Liquid Solutions****Solubility of gases**

- (i) Effect of temperature
- (ii) Effect of pressure

**1. Vapour Pressure****2. Raoult's law**

- (i) When volatile solute is added
  - (a) When solute and solvent; both are miscible
  - (b) When both are immiscible

- (ii) When non-volatile solute is added.

**3. Condensation of vapours of solution****4. Ideal and non-ideal solutions****5. Azeotropic mixtures****Colligative properties (C.P.)****1. Introduction****2. The various C.P.****(i) Lowering of V.P.**

- (a) Determination of molar masses

- (b) It's measurement

**(ii) Boiling point elevation****(iii) Depression in freezing point****(iv) Osmotic pressure**

- (a) Osmosis
- (b) Reverse osmosis
- (c) Isotonic solution

**3. Van't Haff factor; Where the solute associates or dissociates in solution.**

## SOLVED EXAMPLES

### OBJECTIVE

**Q.1** 214.2 gram of sugar syrup contains 34.2 gram of sugar. Calculate (i) molality of the solution and (ii) mole fraction of the sugar in the syrup –

(A) 0.555m, 0.0099 (B) 0.455m, 0.0110 (C) 0.355m, 0.0199 (D) None of these

**Ans.** (A)

**Sol.** (i) Mass of sugar = 34.2 gram. Number of moles of sugar =  $\frac{34.2}{\text{mol. mass}} = \frac{34.2}{342} = 0.1$

Mass of water =  $(214.2 - 34.2) = 180$  gram or  $\frac{180}{1000}$  kg

Number of moles of water =  $\frac{180}{18} = 10$

Molality =  $\frac{\text{No. of moles of sugar}}{\text{Mass of water in kg}} = \frac{0.1}{180} \times 1000 = 0.555 \text{ m}$

(ii) Total no. of moles =  $10.0 + 0.1 = 10.1$

Mole fraction of sugar =  $\frac{\text{No. of moles of sugar}}{\text{Total number of moles}} = \frac{0.1}{10.1} = 0.0099$

**Q.2** Calculate the amount of oxalic acid ( $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ) required to obtain 250 ml of semimolar solution.

(A) 15.75 g (B) 1.575 g (C) 157.5 g (D) None

**Ans.** (A)

**Sol.** Molarity of solution = 0.5 M

Volume of solution = 250 ml

$\therefore$  milli mole oxalic acid =  $M \times V \text{ (ml)} = \frac{1}{2} \times 250$  or  $\frac{w}{M} \times 1000 = 0.5 \times 250$

$\therefore w = \frac{250 \times 126}{2 \times 1000} = 15.75 \text{ g}$

**Q.3** 15 gram of methyl alcohol is dissolved in 35 gram of water. What is the mass percentage of methyl alcohol in solution?

(A) 30% (B) 50% (C) 70% (D) 75%

**Ans.** (A)

**Sol.** Total mass of solution =  $(15 + 35) \text{ gram} = 50 \text{ gram}$

mass percentage of methyl alcohol =  $\frac{\text{Mass of methyl alcohol}}{\text{Mass of solution}} \times 100 = \frac{15}{50} \times 100 = 30\%$

**Q.4** 1.82 g metal required 32.5 mL of N HCl to dissolve it. What is equivalent weight for metal?

(A) 65 (B) 75 (C) 56 (D) 90

**Ans.** (C)



Sol.  $\therefore$  Meq. of metal = Meq. of HCl or  $\frac{1.82}{E} \times 1000 = 32.5 \times 1$   
 $\therefore E = 56$

**Q.5** The vapour pressure of pure liquid 'A' at 310°C is 120 torr. The vapour pressure of this liquid in solution with liquid B is 72 torr. Calculate the mole fraction of 'A' in solution if the mixture obeys Raoult's law.  
 (A) 0.06 (B) 0.9 (C) 0.3 (D) 0.6

**Ans** (D)

**Sol.** Given is vapour pressure of pure component 'A',  $P_A^\circ = 120$  torr

Partial pressure of A,  $P_A = 72$  torr

Suppose its mole fraction in solution is  $X_A$ , then according to Raoult's law.

$$P_A = P_A^\circ \cdot x_A$$

$$72 = 120 \times x_A \text{ or } x_A = \frac{72}{120} = 0.6$$

**Q.6** The degree of dissociation of  $\text{Ca}(\text{NO}_3)_2$  in dilute aqueous solution containing 7.0 g of salt per 100.0 g of water at 100°C is 70%. If the vapour pressure of water at 100°C is 760 mm Hg, the vapour pressure of the solution is

(A) 748.3 mm Hg (B) 1492.6 mm Hg (C) 373.2 mm Hg (D) 74.03 mm Hg

**Ans.** (A)

**Sol.** Moles of  $\text{Ca}(\text{NO}_3)_2 = \frac{7}{168}$  present in 100.0 g of water

Since dissociation is 70%, the total number of particles

$$= \frac{7}{168} \times 0.7 \times 3 = 0.0875 = n$$

$$\text{Also, moles of solvent} = \frac{100}{18} = 5.55 = N$$

Applying Raoult's law

$$\frac{p^\circ - p_{\text{solution}}}{p^\circ} = \frac{n}{n + N}$$

$$\text{Or } \frac{760 - p}{760} = \frac{0.087}{0.087 + 5.55}$$

$$\text{Or } 760 - p = 760 \left[ \frac{0.087}{5.637} \right] = 760[0.0154] = 11.704$$

$$\text{Or } p = 760 - 11.704 = 748.2 \text{ mm Hg}$$

**Q.7** The vapour pressure of a solvent is 20 torr whereas that of its dilute solution is 17 torr. The mole fraction of the solvent is

- (A) 0.6 (B) 0.4 (C) 0.85 (D) 0.7

**Ans.** (C)

**Sol.** Vapour pressure of solvent  $p^\circ = 20$  torr and vapour pressure of solution  $p_s = 17$  torr.

Therefore,  $\frac{p^\circ - p_s}{p^\circ} = \text{mole fraction of solute}$

$$\text{Or } \frac{20 - 17}{20} = 0.15 = \text{mole fraction of solute}$$

$$\text{Mole fraction of solvent} = 1 - 0.15 = 0.85$$

**Q.8** Methyl alcohol and ethyl alcohol have vapour pressure equal to 88.5 mm and 42.0 mm respectively at 45°C. If 16.0 g of methanol and 46.0 g of ethanol are mixed at 45°C, the mole fraction of methanol in the vapour is.....(the mixture may be taken as ideal solution).

- (A) 0.467 (B) 0.502 (C) 0.513 (D) 0.556

**Ans.** (C)

**Sol.** For an ideal solution, obeying Raoult's law, the vapour pressure of mixture

$$p_{\text{mixture}} = p_{\text{methanol}}^\circ \cdot x_{\text{methanol}}^\circ + p_{\text{ethanol}}^\circ \cdot x_{\text{ethanol}}^\circ$$

$$\text{Or } p_{\text{mixture}} = 88.5 \times \frac{16/32}{\frac{16}{32} + \frac{46}{46}} + 42.0 \times \frac{46/46}{\frac{16}{32} + \frac{46}{46}}$$

$$p_{\text{mixture}} = 88.5 \times \frac{0.5}{1.5} + 42.0 \times \frac{1}{1.5} = 57.44 \text{ mm}$$

The mole fraction of any constituent 'i' in vapour phase is

$$= \frac{p_i}{p_{\text{total}}} \text{ that is } \frac{\text{vap. pressure of the constituent in solution}}{\text{Total vap. pressure of solution}}$$

$$= x_i \cdot \frac{p_i^\circ}{p_{\text{total}}} = 88.5 \times \left[ \frac{16/32}{16/32 + 46/46} \right] / 57.44$$

$$\text{Or } \text{the mole fraction of methanol in vapour phase} = 29.47 / 57.44 = 0.5130$$

- Q.9** The vapour pressure of benzene at 80°C is lowered by 10 mm when 2.0 g of a non-volatile substance is dissolved in 78 g of benzene. The vapour pressure of pure benzene at 80°C is 750 mm. The molar mass of the non-volatile substance is

(A) 150 (B) 1050 (C) 1500 (D) 1550

**Ans.** (A)

**Sol.** If  $P^\circ$  is the vapour pressure of pure benzene and  $P$  the vapour pressure of solution,  $w$  the weight of non-volatile substance of molecular mass ' $m$ ' and  $W$  the weight of solvent benzene with molecular mass  $M$ ,

$$\frac{P^\circ - P}{P^\circ} = \frac{w/m}{W/M} = \frac{wM}{Wm} \text{ substituting the values}$$

$$\frac{10}{750} = \frac{2 \times 78}{78 \times m}$$

$$0.0133 = \frac{156}{78 \times m}$$

$$\text{Or } m = \frac{156}{78 \times 0.0133} = 150.37 \sim 150$$

- Q.10** Calculate the molal elevation constant of water evaporates at 100°C with the absorption of 536 calories per gm ( $R = 2 \text{ cal}$ )

(A) 0.519°C (B) 0.0519°C (C) 1.519°C (D) 2.519°C

**Ans.** (A)

**Sol.** Molal elevation constant of the solvent.

$$K_b = \frac{RT_b^2}{l_v \times 1000} = \frac{2 \times 373 \times 373}{536 \times 1000} = 0.519^\circ\text{C}$$

- Q.11** 0.15g of a substance dissolved in 15g of solvent boiled at a temperature higher by 0.216°C than that of the pure solvent. Calculate the molecular weight of the substance. Molal elevation constant for the solvent is 2.16°C.

(A) 216 (B) 100 (C) 178 (D) None of these

**Ans.** (B)

**Sol.** Here it is given that

$$w = 0.15 \text{ g}, \quad \Delta T_b = 0.216^\circ\text{C}$$

$$W = 15 \text{ g}, \quad K_b = 2.16^\circ\text{C} \quad m?$$

$$\text{Substituting values in the expression, } m = \frac{1000 \times K_b \times w}{\Delta T_b \times W} \quad m = \frac{1000 \times 2.16 \times 0.15}{0.216 \times 15} = 100$$

- Q.12** If latent heat of fusion of ice is 80 cal/g at 0°C, calculate molal depression constant for water.

(A) 18.63 (B) 186.3 (C) 1.863 (D) 0.1863

**Ans.** (C)

**Sol.**  $K_f = \frac{RT_f^2}{1000l_f}$  Here  $R = 2 \text{ cal}$ ,  $T_f = 0 + 273 = 273 \text{ K}$ ,  $l_f = 80 \text{ cal}$

$$K_f = \frac{2 \times 273 \times 273}{1000 \times 80} = 1.863$$

**Q.13** Osmotic pressure of a sugar solution at  $24^\circ\text{C}$  is 2.5 atmospheres. Determine the concentration of the solution in gm mole per litre.

(A) 0.0821 moles/litre (B) 1.082 moles/litre (C) 0.1025 moles/litre (D) 0.0827 moles/litre

**Ans.** (C)

**Sol.** Here it is given that

$$\pi = 2.5 \text{ atm}, T = 24 + 273 = 297^\circ\text{A}, S = 0.0821 \text{ lit. atm. deg}^{-1} \text{ mol}^{-1}, C = ?$$

$$\text{We know that } \pi = CST \quad \text{or } C = \frac{\pi}{ST} = \frac{2.5}{0.0821 \times 297} = 0.1025 \text{ moles/litre}$$

**Q.14** Twenty grams of a substance were dissolved in 500 ml. of water and the osmotic pressure of the solution was found to be 600 mm of mercury at  $15^\circ\text{C}$ . Determine the molecular weight of the substance.

(A) 1120 (B) 1198 (C) 1200 (D) None of these

**Ans.** (B)

**Sol.** Here it is given that

$$w = 20 \text{ gm}; V = 500 \text{ ml.} = \frac{500}{1000} = 0.5 \text{ litre}$$

$$\pi = 600 \text{ mm} = \frac{600}{760} \text{ atm}; T = 15 + 273 = 288^\circ\text{A} \quad m = ?$$

According to Van't Hoff equation,

$$\pi V = nST \quad \pi V = \frac{w}{m} ST$$

$$\therefore m = \frac{wST}{\pi V} = \frac{20 \times 0.0821 \times 288 \times 760}{600 \times 0.5} = 1198$$

**Q.15** What weight of NaCl is added to one litre of water so that  $\Delta T_f/K_f = \frac{1}{500}$ ?

(A) 5.85 g (B) 0.585 g (C) 0.0585 g (D) 0.0855 g

**Ans.** (C)

**Sol.** For NaCl  $i = 2$

$$\text{Or } \Delta T_f = i \cdot K_f \cdot m$$

$$\Delta T_f/K_f = 2 \cdot m$$

$$\text{Or } \frac{1}{500} = 2 \times m$$



Or molality =  $\frac{1}{1000}$  or  $\frac{1}{1000}$  moles are dissolved  $\text{Kg}^{-1}$  of water or approximately  $\frac{1}{1000}$  moles are present in 1.0 litre of water (considering molarity and molality to be the same)

$$\therefore \text{Weight of NaCl} = \frac{1}{1000} \times 58.5 \text{ g of NaCl}$$

$$= 0.0585 \text{ g of NaCl.}$$

### SUBJECTIVE

- Q.16** The addition of 3 gm of substance to 100 gm  $\text{CCl}_4$  ( $M = 154 \text{ gm mol}^{-1}$ ) raises the boiling point of  $\text{CCl}_4$  by  $0.60^\circ\text{C}$ .  $K_b$  of  $\text{CCl}_4$  is  $5.03 \text{ kg mol}^{-1} \text{ K}$ . Calculate
- the freezing point depression
  - the relative lowering of vapour pressure
  - the osmotic pressure at 298 K
  - the molar mass of the substance

Given  $K_f(\text{CCl}_4) = 31.8 \text{ kg mol}^{-1} \text{ K}$  and  $\rho$  (density) of solution =  $1.64 \text{ gm/cm}^3$

**Ans.** (a)  $3.79^\circ\text{C}$ , (b) 0.018, (c) 4.65 atm, (d) 251.5

**Sol.** (a)  $0.60 = K_b \times m$   
 $\Delta T_f = K_f \times m$   
 $\frac{\Delta T_f}{0.60} = \frac{K_f}{K_b} \Rightarrow \frac{31.8}{5.03}$   
 $\Delta T_f = 3.79^\circ\text{C}$  **Ans.**

(b)  $m = \frac{\Delta T_b}{K_b} = \frac{0.60}{5.03} = 0.12$

$$n_{\text{solute}} = 0.12, n_{\text{solvent}} = \frac{1000}{154} = 6.49$$

$$\text{Relative lowering of V.P.} = \frac{n_{\text{solute}}}{n_{\text{solvent}}} = \frac{0.12}{6.49} = 0.018 \text{ Ans.}$$

- (c) Amount of solute in 100 gm of solvent = 3 gm  
 Amount of solute in 1000 gm of solvent = 30 gm

$$W_{\text{solution}} = 1030 \text{ gm}, V_{\text{solution}} = \frac{1030}{\rho_{\text{solution}}} = \frac{1030}{1.64} \text{ cm}^3 = \frac{1030}{1640} \text{ litre}$$

$$\pi = \frac{n_{\text{solute}} RT}{V_{\text{solution}}}$$

$$= \frac{0.12 \times 0.082 \times 298}{\frac{1030}{1640}} = 4.65 \text{ (atm) Ans.}$$

$$(d) \quad 0.12 = \frac{30}{m_{\text{solute}}}$$

$$m_{\text{solute}} = \frac{3000}{0.12} = 250 \text{ (app) Ans.}$$

**Q.17** Vapour pressure of  $C_6H_6$  and  $C_7H_8$  mixture at  $50^\circ C$  is given by  $P \text{ (mm Hg)} = 180 X_B + 90$ , where  $X_B$  is the mole fraction of  $C_6H_6$ . A solution is prepared by mixing 936 g benzene and 736 g toluene and if the vapours over this solution are removed and condensed into liquid and again brought to the temperature of  $50^\circ C$ , what would be the new mole fraction of  $C_6H_6$  in the vapour state?

**Ans.** 0.93

**Sol.**  $C_6H_6 - B$ ,  $C_7H_8 - T$

$$n_B = \frac{936}{78}, \quad n_T = \frac{736}{92} = 8$$

$$X_B = \frac{n_B}{n_B + n_T} = \frac{12}{12 + 8} = 0.6$$

$$P = 180 X_B + 90$$

Now  $P = (P_B^0 - P_T^0) X_B + P_T^0$

$$P_A^0 = 90 \text{ mm,}$$

$$P_T^0 = 270 \text{ mm}$$

$$P_T = 0.6 \times 270,$$

$$P = 180 \times 0.6 + 90$$

$$= 162 \text{ mm}$$

$$= 198 \text{ mm}$$

$$Y_B = \frac{P_B}{P} = \frac{162}{198} = \frac{9}{11}$$

Mole fraction of benzene in vapour

Now on condensation

$$X_B = Y_B \quad X_B = \frac{9}{11}$$

$$P_B = \frac{9}{11} \times 270 \text{ mm,} \quad P = 180 \times \frac{9}{11} + 90 = 90 \left( \frac{29}{11} \right) \text{ mm}$$

$$X_B = \frac{P_B}{P} = \frac{\frac{9}{11} \times 270}{90 \times \frac{29}{11}} = \frac{27}{29} = 0.93 \text{ Ans.}$$

**Q.18** The vapour pressure of two pure liquids, A and B that form an ideal solution are 300 and 800 torr respectively, at temperature T. A mixture of the vapour of A and B for which the mole fraction of A is 0.25 is slowly compressed at temperature T. Calculate

- the composition of the first drop of the condensate,
- the total pressure when this drop is formed,
- the composition of the solution whose normal boiling point is T,
- the pressure when only the last bubble of vapour remains, and
- the composition of the last bubble.

**Ans.** (a) 0.47, (b) 565 torr, (c)  $x_A = 0.08$ ,  $x_B = 0.92$ , (d) 675 torr, (e)  $x'_A = 0.11$ ,  $x'_B = 0.89$

**Sol.** (a)  $P_A = X_A \times P_A^0$   
 $P_T = X_A (P_A^0 - P_B^0) + P_B^0$   
 $564.7 = X_A (300 - 800) + 800$   
 $X_A = 0.47$  **Ans.**

(b)  $\frac{Y_A}{P_A^0} + \frac{Y_B}{P_B^0} = \frac{1}{P_T}$   
 $\frac{0.25}{300} + \frac{0.75}{800} = \frac{1}{P_T}$   
 $P_T = 564.7$  **torr**

(c) At boiling temp vapour pressure = 760 torr  
 $300 X_A + 800 X_B = 760$   
 $X_A (300 - 800) + 800 = 760$   
 $X_A = 0.08$   
 $X_B = 0.92$

(d) When only the last bubble of vapour remains, we can assume that the composition of vapour is now the composition of the condensation

$$\therefore X_A = 0.25, \quad X_B = 0.75$$

$$P_T = X_A P_A^0 + X_B P_B^0$$

$$= 0.25 \times 300 + 0.75 \times 800$$

$$= 675 \text{ torr}$$

(e) Composition of last bubble =  $X_A$   
 $X_A = Y_A$

$$X_A = \frac{P_A}{P_T}$$

$$X_A = \frac{75}{675} = 0.11, \quad X_B = 1 - 0.11 = 0.89$$

**Q.19** When the mixture of two immiscible liquids (water and nitrobenzene) boils at 372 K and the vapour pressure at this temperature are 97.7 kPa ( $H_2O$ ) and 3.6 kPa ( $C_6H_5NO_2$ ). Calculate the weight % of nitrobenzene in the vapour.

**Ans.** 20.11 %

**Sol.** Let vapour contains  $W_1$  gm of  $C_6H_5NO_2$  and  $W_2$  gm of  $H_2O$

$$n_1 = \frac{w_1}{123}, \quad n_2 = \frac{w_2}{18}$$

for gases

Ratio of moles = Ratio of pressure

$$n_1 : n_2 = 3.6 : 97.7$$

$$\frac{w_1}{123} \times \frac{18}{w_2} = \frac{3.6}{97.7}$$

$$\frac{w_1}{w_2} = \frac{3.6 \times 123}{18 \times 97.7} = 0.252$$

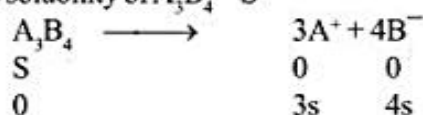
$$w_2 = w \text{ (let)}, w_1 = 0.252 w$$

$$\begin{aligned} \% w_1 &= \frac{0.252w}{1.252w} \times 100 \\ &= 20.11 \% \text{ Ans.} \end{aligned}$$

**Q.20** A very dilute saturated solution of a sparingly soluble salt  $A_3B_4$  has a vapour pressure of 20 mm of Hg at temperature T, while pure water exerts a pressure of 20.0126 mm Hg at the same temperature. Calculate the solubility product constant of  $A_3B_4$  at the same temperature.

**Ans.**  $5.4 \times 10^{-13}$

**Sol.** Let the solubility of  $A_3B_4 = S$



$$\text{Solubility product of } A_3B_4 (K_{sp}) = (3S)^3 (4S)^4 = 6912 S^7$$

$$\text{For } A_3B_4, i = 7$$

To solve this problem we will assume

Molarity = Molality and  $w_{\text{solvent}} = w_{\text{solution}}$

Molality of  $A_3B_4 = S$

$$\Rightarrow n_{\text{solute}} = S, w_{\text{solvent}} = 1000 \text{ gm}$$

$$n_{\text{solvent}} = \frac{1000}{18} = 55.56$$

$$\frac{P_{\text{solvent}}^0 - P_{\text{solution}}}{P_{\text{solvent}}^0} = i \times \frac{n_{\text{solute}}}{n_{\text{solvent}}}$$

$$\frac{20.0126 - 20}{20.0126} = \frac{5 \times 7}{55.56}$$

$$S = 5 \times 10^{-3} \text{ M}$$

$$\begin{aligned} \therefore \text{Solubility product of } A_3B_4 (K_{sp}) &= 6912 S^7 \\ &= 6912 \times 5^7 \times 10^{-21} = 5.4 \times 10^{-13} \end{aligned}$$

**Q.21** If the apparent degree of ionization of KCl in water at 290 K is 0.86. Calculate the mass of KCl which must be made up to 1 dm<sup>3</sup> of aqueous solution to the same osmotic pressure as the 4.0% solution of glucose at that temperature.

**Ans.** 8.9 gm

**Sol.** Glucose ( $C_6H_{12}O_6$ ),

$$\text{Molar concentration of glucose solution. } (C_1) = \frac{4.0 \times 1000}{180 \times 100} = \frac{2}{9} \text{ M}$$

$$\pi_1 = C_1 RT = \frac{2}{9} RT$$

For KCl solution.

$$n = 2, \alpha = 0.86,$$

$$i = 1 + (n - 1) \alpha$$

$$i = 1.86$$



w = amount of KCl present in 1 dm<sup>3</sup> solution.

$\pi_2$  = Osmotic pressure of KCl solution

$$\pi_2 = 1.86 \times \frac{w RT}{74.5 \times 1}$$

$$\pi_1 = \pi_2$$

$$\frac{9}{2} RT = \frac{1.86 w RT}{74.5}$$

$$W = \frac{2 \times 74.50}{9 \times 1.86}$$

$$w = 8.9 \text{ gm}$$

$\therefore$  Mass of KCl present in 1 dm<sup>3</sup> of aq. solution = 8.9 gm

**Q.22** The specific conductivity of a 0.5 M aq. solution of monobasic acid HA at 27°C is 0.006 S cm<sup>-1</sup>. It's molar conductivity at infinite dilution is 200 S cm<sup>2</sup> mol<sup>-1</sup>. Calculate osmotic pressure (in atm) of 0.5 M HA (aq) solution at 27°C. Given R = 0.08 L-atm/K-mol

**Ans.** 12.72

**Sol.**  $\Lambda_m^c = \frac{K \times 1000}{C} = \frac{0.006 \times 1000}{0.500} = 12 \text{ S cm}^2 \text{ mol}^{-1}$

$$\Lambda_m^0 = 200 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\alpha = \frac{\Lambda_m^c}{\Lambda_m^0} = 0.06$$

for HA, n = 2

$$\begin{aligned} i &= 1 + (n - 1) \alpha \\ &= 1 + (2 - 1) \times 0.6 \\ i &= 1.06 \end{aligned}$$

$$\begin{aligned} \pi &= i \times CRT \\ &= 1.06 \times 0.5 \times 0.082 \times 300 \\ \pi &= 12.72 \text{ atm} \end{aligned}$$

**Q.23** The freezing point of 0.02 mol fraction solution of acetic acid (A) in benzene (B) is 277.4K. Acetic acid exists partly as a dimer  $2A \rightleftharpoons A_2$ . Calculate equilibrium constant for the dimerisation. Freezing point of benzene is 278.4 K and its heat of fusion is 10.042 kJ mol<sup>-1</sup>.

**Ans.** K = 3.22

**Sol.**  $X_B = 0.02 \Rightarrow n_B = 0.02 \text{ and } n_A = 0.98$   
 $W_A = 0.98 \times 78 \text{ gm}$

$$\text{Molality (m)} = \frac{n_B \times 1000}{W_A} = \frac{0.02 \times 1000}{0.98 \times 78} = 0.2616$$

$$\begin{aligned} K_f &= \frac{RT_f^2 m_A}{\Delta_f H \times 1000} = \frac{8.314 \times (278.4)^2 \times 78}{10042 \times 1000} \\ &= 5.00 \text{ K/m} \end{aligned}$$

$$\Delta T_f = i \times K_f m$$

$$1 = i \times 5 \times 0.2616$$

$$i = \frac{1}{5 \times 0.2616}$$

$$= 0.7645$$

$$i = 1 + \left( \frac{1}{n} - 1 \right) \alpha$$

As acetic acid dimerise,  $n = 2$

$$i = 1 - \frac{\alpha}{2}$$

$$0.7645 = 1 - \frac{\alpha}{2}$$

$$\alpha = 0.4710$$

We assume : Molarity = Molality

$$\therefore \text{Molarity (C)} = 0.2616$$



$$\text{At } t = 0 \quad C \quad 0$$

$$\text{At equi.} \quad C(1 - \alpha) \quad \frac{C\alpha}{2}$$

$$K = \frac{[A_2]}{[A]^2} = \frac{C\alpha}{2C^2(1-\alpha)^2} = \frac{\alpha}{2C(1-\alpha)^2} = \frac{0.471}{2 \times 0.2616 (0.529)^2} = 3.22$$

**Q.24** 1kg of an aqueous solution of Sucrose is cooled and maintained at  $-4^\circ\text{C}$ . How much ice will be separated out if the molality of the solution is 0.75?  $K_f(\text{H}_2\text{O}) = 1.86 \text{ Kg mol}^{-1}\text{K}$ .

**Sol.** Since molality of solution is .75,  
hence .75 moles of sucrose are present in 1000 g of solvent (i.e. water)

$$\therefore m_{\text{solution}} = m_{\text{water}} + m_{\text{sucrose}} = 1000 + .75 \times 342 = 1256.5 \text{ gm}$$

$$\therefore m_{\text{sucrose}} (\text{in kg}) = \frac{256.5}{1256.5} \times 1000 = 204.14 \text{ gm}, \quad m_{\text{water}} = 1000 - 204.14 = 795.86 \text{ gm}$$

$$\therefore \Delta T_f = K_f \times m \quad \Rightarrow 4 = 1.86 \times \frac{204.14/342}{W/1000} \quad \Rightarrow w = 277.15$$

$$\therefore \text{amount of ice} = 795.86 - 277.15 = 518.31 \text{ gm}$$

- Q.25** River water is found to contain 11.7% NaCl, 9.5%  $\text{MgCl}_2$ , and 8.4%  $\text{NaHCO}_3$  by weight of solution. Calculate its normal boiling point assuming 90% ionization of NaCl, 70% ionization of  $\text{MgCl}_2$  and 50% ionization of  $\text{NaHCO}_3$  ( $K_b$  for water = 0.52)

**Sol.**  $n_{\text{NaCl}} = \frac{11.7}{58.5} = 0.2, \quad n_{\text{MgCl}_2} = \frac{9.5}{95} = 0.1, \quad n_{\text{NaHCO}_3} = \frac{8.4}{84} = 0.1$

$i_{\text{NaCl}} = 1 + \alpha = 1 + 0.9 = 1.9, \quad i_{\text{MgCl}_2} = 1 + 2\alpha = 1 + 0.7 \times 2 = 2.4,$

$i_{\text{NaHCO}_3} = 1 + 2\alpha = 1 + 0.5 \times 2 = 2.0$

Weight of solvent =  $100 - (11.7 + 9.5 + 8.4) = 70.4 \text{ g}$

$$\Delta T_b = \frac{(i_{\text{NaCl}} \times n_{\text{NaCl}} + i_{\text{MgCl}_2} \times n_{\text{MgCl}_2} + i_{\text{NaHCO}_3} \times n_{\text{NaHCO}_3}) \times K_b \times 1000}{\text{Weight of solvent}}$$

$$= \frac{(1.9 \times 0.2 + 2.4 \times 0.1 + 2 \times 0.1) \times 0.52 \times 1000}{70.4} = 5.94^\circ\text{C}$$

$\therefore$  Boiling point of solution =  $100 + 5.94 = 105.94^\circ\text{C}$

- Q.26** An aqueous solution containing 288 gm of a non-volatile compound having the stoichiometric composition  $\text{C}_x\text{H}_{2x}\text{O}_x$  in 90 gm water boils at  $101.24^\circ\text{C}$  at 1.00 atmospheric pressure. What is the molecular formula?

$K_b(\text{H}_2\text{O}) = 0.512 \text{ K mol}^{-1} \text{ kg } T_b(\text{H}_2\text{O}) = 100^\circ\text{C}$

**Sol.** Elevation in B.P. =  $101.24 - 100 = 1.24^\circ\text{C}$

$$\Delta T_b = K_b \times i \times \text{molality} \Rightarrow 1.24 = 0.512 \times \frac{288}{m} \times \frac{1000}{90} \quad (\therefore i = 1)$$

$\therefore m = 1321.2 \text{ gm mol}^{-1}$

molar mass of  $\text{C}_x\text{H}_{2x}\text{O}_x = 12x + 1 \times 2x + 16x = 30x$

$\therefore 30x = 1321.2$

$\therefore x = 44$

Hence the molecular formula is  $= \text{C}_{44}\text{H}_{88}\text{O}_{44}$

- Q.27** 30 ml of  $\text{CH}_3\text{OH}$  ( $d = 0.7980 \text{ gm cm}^{-3}$ ) and 70 ml of  $\text{H}_2\text{O}$  ( $d = 0.9984 \text{ gm cm}^{-3}$ ) are mixed at  $25^\circ\text{C}$  to form a solution of density  $0.9575 \text{ gm cm}^{-3}$ . Calculate the freezing point of the solution.  $K_f(\text{H}_2\text{O})$  is  $1.86 \text{ K g mol}^{-1}$ . Also calculate its molarity

**Sol.** Weight of  $\text{CH}_3\text{OH}$  ( $w_1$ ) =  $30 \text{ cm}^3 \times 0.7980 \text{ gm/cm}^3 = 23.94 \text{ gm}$

Weight of solvent ( $\text{H}_2\text{O}$ ) ( $w_2$ ) =  $70 \text{ cm}^3 \times 0.9984 \text{ gm cm}^3 = 69.888 \text{ gm}$

$$m = \frac{23.94}{32} \times \frac{1000}{69.88} = 10.7046 \text{ molal}$$

$\therefore \Delta T_f = K_f \times i \times \text{molality}, \quad (\text{for } \text{CH}_3\text{OH}, i = 1)$

$\Delta T_f = 1.86 \times 10.7046^\circ\text{C} = 19.91^\circ\text{C}$

Freezing point of the solution =  $0 - 19.91^\circ\text{C} = -19.91^\circ\text{C}$

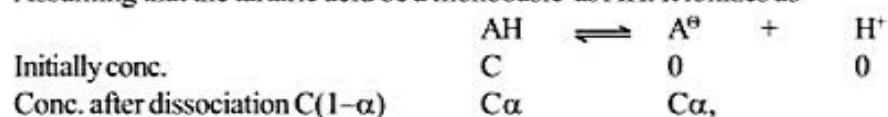
Weight of solution = weight of solute + weight of solvent =  $23.94 + 69.888 = 93.828 \text{ gm}$

$$\text{volume of the solution} = \frac{\text{wt. of the solution}}{\text{density of the solution}} = \frac{93.828}{0.95751} = 97.99 \text{ ml}$$

$$M (\text{molarity}) = \frac{23.94}{32} \times \frac{1000}{97.99} \text{ mol lit}^{-1} = 7.63 \text{ M}$$

**Q.28** Find  $K_a$ , the ionization constant of tartaric acid if a 0.100 molal aqueous solution of tartaric acid freezes at  $-0.205^\circ\text{C}$ . Assume that only the first ionization is of importance and that  $0.1\text{ m} = 0.1\text{ M}$ .  $K_f = 1.86\text{ kg mol}^{-1}\text{ K}$ .

**Sol.** Assuming that the tartaric acid be a monobasic as AH. It ionizes as



Here,  $i = \frac{\text{C}(1-\alpha) + \text{C}\alpha + \text{C}\alpha}{\text{C}}$ , where  $\alpha = \text{degree of dissociation} = \frac{\text{C}(1+\alpha)}{\text{C}} = 1+\alpha$

Molal concentration = 0.1

$$\Delta T_f = K_f \times C_m \times i \quad \Rightarrow \quad 0.205 = 1.86 \times 0.1 \times (1+\alpha) \quad \therefore \alpha = 0.1$$

$$K_a = \frac{[\text{A}^\ominus][\text{H}^+]}{[\text{AH}]} = \frac{\text{C}\alpha \times \text{C}\alpha}{\text{C}(1-\alpha)} = \frac{\alpha^2 \text{C}}{1-\alpha} \quad K_a = \frac{(0.1)^2 \times 0.1}{1-0.1} = 1.11 \times 10^{-3}$$

$$\therefore K_a = 1.11 \times 10^{-3}$$



## ELECTRO-CHEMISTRY

### ELECTROCHEMICAL CELLS

An electrochemical cell consists of two electrodes (metallic conductors) in contact with an electrolyte (an ionic conductor).

An electrode and its electrolyte comprise an **Electrode Compartment**.

Electrochemical Cells can be classified as:

- (i) **Electrolytic Cells** in which a non-spontaneous reaction is driven by an external source of current.
- (ii) **Galvanic Cells** which produce electricity as a result of a spontaneous cell reaction

#### Electrochemical cell :

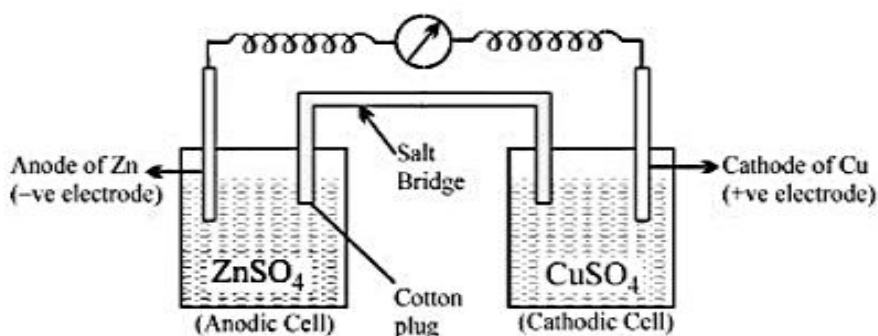
An electrochemical cell is a system consisting of electrodes that dip into an electrolyte and in which a chemical reaction either uses or generates an electric current.

A voltaic or galvanic cell is an electrochemical cell in which a spontaneous reaction generates an electric current.

A voltaic cell consists of two half-cells that are electrically connected. Each half cell is the portion of an electrochemical cell in which a half cell -reaction take place.

A simple half-cell can be made from a metal strip that dips into a solution of its metal ion. An example is the zinc-zinc ion half-cell (often called simply a zinc electrode), which consists of a zinc metal strip dipping into a solution of a zinc ion salt. Another simple half-cell consists of a copper metal strip dipping into a solution of a copper ion salt (copper electrode).

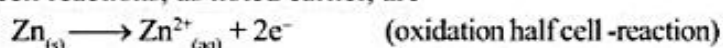
In a voltaic cell, two half-cells are connected in such a way that electrons flow from one metal electrode to another through an external circuit, and ions flow from one half-cell to another through an internal cell connection. Figure given below illustrates an atomic view of a voltaic cell consisting of a zinc electrode and a copper electrode. As long as there is an external circuit, electrons can flow through it from one electrode to another. Because zinc tends to lose electrons more readily than copper, zinc atoms in the zinc electrode lose electrons to produce zinc ions. These electrons flow through the external circuit to the copper electrode, where they react with the copper ions to produce copper metal, and an electric current flows through the external circuit.



The two half-cells must be connected internally to allow ions to flow between them. As zinc ions continue to be produced, the zinc ion solution begins to build up a positive charge. Similarly, as copper ions plate on as copper, the solution builds up a negative charge. The half cell reactions will stop unless positive ions can move from the zinc half-cell to the copper half cell, and negative ions from the copper half-cell can move to the zinc half-cell. It is necessary that these ion flow occur without mixing of the zinc ion and copper ion solutions. If copper ion come in contact with the zinc metal, for example, direct reaction would occur without an electric current being generated. The voltage would drop, and the battery would run down quickly.

The two half-cells of a voltaic cell are connected by a salt bridge. A salt bridge is a tube of an electrolyte in a gel that is connected to the two half-cells of a voltaic cell; the salt bridge allows the flow of ions but prevents the mixing of the different solutions that would allow direct reaction of the cell reactants. The half-cells are connected externally so that an electric current flows.

The two half-cell reactions, as noted earlier, are



The first half cell -reaction, in which a species loses electrons, is the oxidation half cell-reaction. The electrode at which oxidation occurs is called the anode. The second half-reaction which a species gains electrons, is the reduction half cell-reaction. The electrode at which reduction occurs is called the cathode. These definitions of anode and cathode hold for all electrochemical cells, including electrolytic cells.

Note that the sum of the two half cell-reaction



The net reaction that occurs in the voltaic cell, it is called the cell reaction.

Once you know which electrode is the anode and which is the cathode, you can determine the direction of electron flow in the external portion of the circuit. Electrons are given up by the anode (from the oxidation half-reaction) and thus flow from it, whereas electrons are used up by the cathode (by the reduction half-reaction) and so flow into this electrode. The anode in a voltaic cell has a negative sign, because electrons flow from it. The cathode in a voltaic cell has a positive sign.



**Note :**

1. The salt-bridge contains solution of strong ionic salts like NaCl, NaNO<sub>3</sub>, KNO<sub>3</sub>, KCl etc., which is soaked in a colloidal solution of agar-agar gel which permits the movement of ions of salts only.
2. Salt bridge carries whole of the current across the boundary ; more over the K<sup>+</sup> and NO<sub>3</sub><sup>-</sup> ions have same speed. Hence, salt bridge with uniform and same mobility of cations and anions completes the electrical circuit & permits the ions to migrate.
3. It maintains the electrical neutrality of the solutions in the two half-cells. In the absence of salt bridge, a reverse potential difference is set up in the two half-cells which results in breaking the continuous supply of voltage.

**In a galvanic cell, cathode is positive with respect to anode.**



## REPRESENTATION OF A CELL ( IUPAC CONVENTIONS)

Let us illustrate the convention taking the example of Daniel cell.

- (i) Anodic half cell is written on left and cathodic half cell on right hand side.  

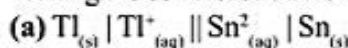
$$\text{Zn(s)} | \text{ZnSO}_4(\text{sol}) || \text{CuSO}_4(\text{sol}) | \text{Cu(s)}$$
- (ii) Two half cells are separated by double vertical lines: Double vertical lines indicate salt bridge or any type of porous partition.
- (iii) EMF (electromotive force) may be written on the right hand side of the cell.
- (iv) Single vertical lines indicate the phase separation between electrode and electrolyte solution.  

$$\text{Zn} | \text{Zn}^{2+} || \text{Cu}^{2+} | \text{Cu}$$
- (v) Inert electrodes are represented in the bracket  

$$\text{Zn} | \text{ZnSO}_4 || \text{H}^+ | \text{H}_2, (\text{Pt})$$

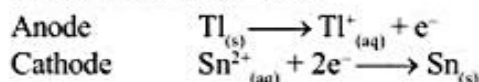
### Illustration

1. Writing the cell Reaction from the Cell Notation

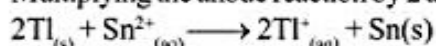


Problem strategy: The cell notation gives the species involved in each half-reaction. When you are going to add half cell- reaction balance half cell reaction in such a way that both have same number of electron.

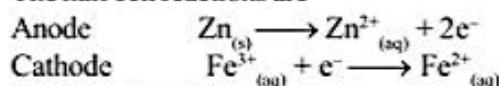
- Sol.** (a) The half-cell reactions are



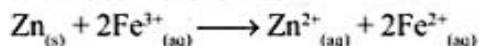
Multiplying the anode reaction by 2 and then summing the half-cell reactions gives



- (b) The half cell reactions are

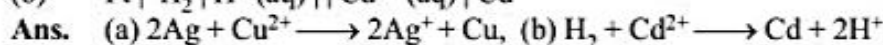
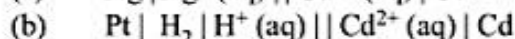
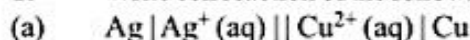


and the cell reaction is:

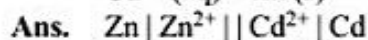
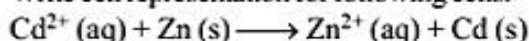


### Exercise

1. Write cell reaction of the following cells :



2. Write cell representation for following cells:

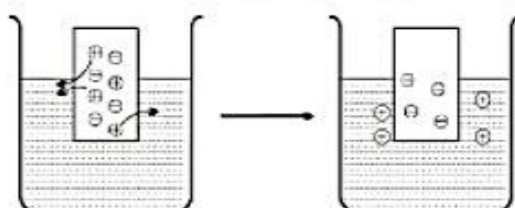


## ELECTRODE POTENTIAL

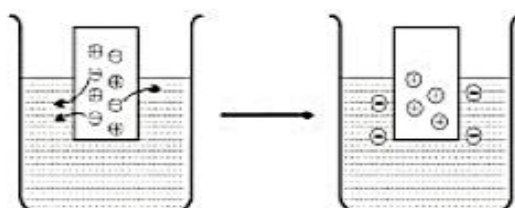
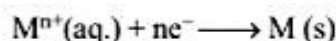
When a metal is placed in a solution of its ions, the metal acquires either a positive or negative charge with respect to the solution. On account of this, a definite potential difference is developed between the metal and the solution. This potential difference is called **electrode potential**.

The potential difference is established due to the formation of electrical double layer at the interface of metal and the solution. The development of negative charge (as on zinc plate) or positive charge (as on copper plate) can be explained in the following manner.

(a) **Oxidation** : Metal ions pass from the electrode into solution leaving an excess of electrons and thus a negative charge on the electrode.



(b) **Reduction** : Metal ions in solution gain electrons from the electrode leaving a positive charge on the electrode.



The magnitude of the electrode potential of a metal is a measure of its relative tendency to undergo oxidation (loss of electrons) or reduction (gain of electrons). The magnitude of potential depends on the following factors :

- (i) Nature of the electrode
- (ii) Concentration of the ion in solution
- (iii) Temperature.

Depending on the nature of the metal electrode to lose or gain electrons, the electrode potential may be of two types :

- (i) **Oxidation potential** : When electrode is negatively charged with respect to solution, i.e., it acts as anode. Oxidation occurs.



- (ii) **Reduction potential** : When electrode is positively charged with respect to solution. i.e., it acts as cathode. Reduction occurs.



it is not possible to measure the absolute value of the single electrode potential directly. Only the difference in potential between two electrodes can be measured experimentally.



## CONCEPT OF ELECTROMOTIVE FORCE (EMF) OF A CELL

Electron flows from anode to cathode in external circuit due to a pushing effect called or electromotive force (e.m.f.). EMF is called as *cell potential*. Unit of e.m.f. of cell is volt.

EMF of cell may be calculated as :

$$E_{\text{cell}} = \text{Reduction potential of cathode} - \text{Reduction potential of anode}$$

Similarly, standard e.m.f. of the cell ( $E^\circ$ ) may be calculated as

$$E^\circ_{\text{cell}} = \text{Standard reduction potential of cathode} - \text{Standard reduction potential of anode}$$

$$E_{\text{cell}} = \text{R.P. (Cathode)} - \text{R.P. (Anode)}$$

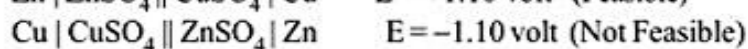
$$= \text{R.P. (Cathode)} + \text{O.P. (Anode)}$$



Which electrode of a galvanic cell corresponds to the higher potential energy.

## SIGN CONVENTION OF EMF

EMF of cell should be positive other wise it will not be feasible in the given direction .



### Illustration

1. For the cell reaction  $2\text{Ce}^{4+} + \text{Co} \longrightarrow 2\text{Ce}^{3+} + \text{Co}^{2+}$

$E^\circ_{\text{cell}}$  is 1.89 V. If  $E^\circ_{\text{Co}^{2+}|\text{Co}}$  is  $-0.28$  V, what is the value of  $E^\circ_{\text{Ce}^{4+}|\text{Ce}^{3+}}$  ?

Ans. 1.61 V

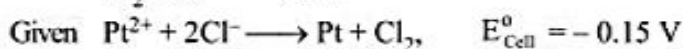
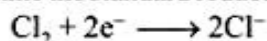
Sol.  $E^\circ_{\text{Cell}} = E^\circ_{\text{Ce}^{4+}|\text{Ce}^{3+}} - E^\circ_{\text{Co}^{2+}|\text{Co}}$

$$1.89 = E^\circ_{\text{Ce}^{4+}|\text{Ce}^{3+}} - (-.28)$$

$$E^\circ_{\text{Ce}^{4+}|\text{Ce}^{3+}} = 1.61\text{V}$$

### Exercise

1. Determine the standard reduction potential for the half reaction :



Ans. 1.35 V

## RELATIONSHIP BETWEEN $\Delta G$ AND ELECTRODE POTENTIAL

Let  $n$ , Faraday charge is taken out from a cell of e.m.f. ( $E$ ), then electrical work done by the cell may be calculated as,

$$\text{Work done} = \text{Charge} \times \text{Potential} = nFE$$

From thermodynamics, we know that decrease in Gibbs free energy of a system is a measure of reversible or maximum obtainable work by the system.

$$\therefore \Delta G = -nFE$$

$$\text{Under standard state} \quad \Delta G^0 = -nFE^0 \quad (i)$$

- (i) From thermodynamics we know,  $\Delta G$  = negative for spontaneous process. Thus from eq.(i) it is clear that the EMF should be +ve for a cell process to be feasible or spontaneous.
- (ii) When  $\Delta G$  = positive,  $E$  = negative and the cell process will be non spontaneous.

Reactions	$\Delta G$	$E$
Spontaneous	(-)	(+)
Non- spontaneous	(+)	(-)
Equilibrium	0	0

Standard free energy change of a cell may be calculated by electrode potential data.

Substituting the value of  $E^0$  (i.e., standard reduction potential of cathode- standard reduction potential of anode) in eq. (i) we may get  $\Delta G^0$ .

## NERNST EQUATION

Walter Nemst derived a relation between cell potential and concentration or Reaction quotient.

$$\Delta G = \Delta G^0 + RT \ln Q \quad \dots(1)$$

where  $\Delta G$  and  $\Delta G^0$  are free energy and standard free energy change; 'Q' is reaction quotient.

$$\therefore -\Delta G = nFE \quad \text{and} \quad -\Delta G^0 = nFE^0$$

Thus from Eq. (i), we get  $-nFE = -nFE^0 + RT \ln Q$

$$\text{At } 25^\circ\text{C, above equation may be written as } E = E^0 - \frac{0.0591}{n} \log Q$$

Where 'n' represents number of moles of electron involved in process.

In general, for a redox cell reaction involving the transference of  $n$  electrons

$aA + bB \longrightarrow cC + dD$ , the EMF can be calculated as:

$$E_{\text{Cell}} = E^0_{\text{Cell}} - \frac{0.0591}{n} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

**Illustration**

1. Calculate the EMF of a Daniel cell when the concentration of  $\text{ZnSO}_4$  and  $\text{CuSO}_4$  are 0.001 M and 0.1M respectively. The standard EMF of the cell is 1.1V.

Ans.  $E = 1.159\text{V}$

Sol.  $\text{Zn(S)} + \text{CuSO}_4 \rightarrow \text{ZnSO}_4 + \text{Cu}$

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{.0591}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} = 1.1 - \frac{.0591}{2} \log \frac{10^{-3}}{10^{-1}} = 1.159 \text{ V}$$

**Exercise**

1. The EMF of the cell  $\text{M} | \text{M}^{n+} (0.01\text{M}) || \text{H}^+ (1\text{M}) | \text{H}_2(\text{g}) (1 \text{ atm}), \text{Pt}$  at  $25^\circ\text{C}$  is 0.82V. Calculate the valency of the metal if the standard oxidation potential of the metal is 0.76V.

Take  $\frac{2.303 RT}{F} = 0.06$  at  $25^\circ\text{C}$ .

Ans.  $n = 2$



What will happen to the cell emf as cell start operating from standard condition.

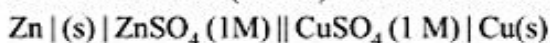


Can the Nernst equation be used at temperature other than room temperature ? What will happen to cell emf as temperature is increased slightly ?

**THERMODYNAMIC TREATMENT OF NERNST EQUATION**

- (i) Prediction and feasibility of spontaneity of a cell reaction.

Let us see whether the cell (Daniel) is feasible or not: i.e. whether Zinc will displace copper or not.



$$E_{\text{Zn}^{2+}/\text{Zn}}^0 = -0.76\text{volt} ; E_{\text{Cu}^{2+}/\text{Cu}}^0 = +0.34\text{volt}$$

$$\begin{aligned} E_{\text{cell}}^0 &= E_{\text{Cu}^{2+}/\text{Cu}}^0 - E_{\text{Zn}^{2+}/\text{Zn}}^0 \\ &= 0.34 - (-0.76) = +1.10 \text{ volt} \end{aligned}$$

Since  $E^0 = +ve$ , hence the cell will be feasible and zinc will displace copper from its salt solution. In the other words zinc will reduce copper.

(ii) **Determination of equilibrium constant :** We know, that

$$E = E^0 - \frac{0.0591}{n} \log Q \quad \text{..(i)}$$

At equilibrium, the cell potential is zero because cell reactions are balanced, i.e.  $E = 0$

$\therefore$  From Eq. (i), we have

$$0 = E^0 - \frac{0.0591}{n} \log K_{eq} \quad \text{or} \quad K_{eq} = \text{anti log} \left[ \frac{nE^0}{0.0591} \right]$$

### Illustration

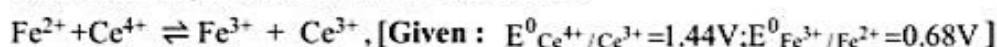
1. Calculate  $E^0$  and  $E$  for the cell  $\text{Sn} | \text{Sn}^{2+} (1\text{M}) || \text{Pb}^{2+} (10^{-3}\text{M}) | \text{Pb}$ ,  $E^0 (\text{Sn}^{2+} | \text{Sn}) = -0.14\text{V}$ ,  $E^0 (\text{Pb}^{2+} | \text{Pb}) = -0.13\text{V}$ . Is cell reaction is feasible?

Ans. No,  $E_{\text{cell}} = -0.078\text{V}$

Sol. 
$$E_{\text{Cell}} = -E_{\text{Sn}^{2+}/\text{Sn}}^0 + E_{\text{Pb}^{2+}/\text{Pb}}^0 - \frac{0.059}{2} \log \left[ \frac{[\text{Sn}^{2+}]}{[\text{Pb}^{2+}]} \right] = +0.14 - 0.13 - \frac{0.059}{2} \log 10^3$$

$$= +0.01 - \frac{0.059}{2} \times 3 = -0.078\text{V} \quad \text{Cell will not work}$$

2. Calculate the equilibrium constant for the reaction



Take  $\frac{2.303 RT}{F} = 0.06$  at  $25^\circ\text{C}$ ,  $\log 4.68 = 0.67$

Ans.  $K_c = 4.68 \times 10^{12}$

Sol.  $\text{Fe}^{2+} + \text{Ce}^{4+} \rightleftharpoons \text{Fe}^{3+} + \text{Ce}^{3+}$

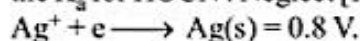
$$E^0 = 1.44 - 0.68 = 0.76\text{V} = \frac{0.06}{1} \log K_c \quad K_c = 4.64 \times 10^{12}$$

### Exercise

1. For the galvanic cell :  $\text{Ag} | \text{AgCl(s)} | \text{KCl} (0.2\text{M}) || \text{KBr} (0.001\text{M}) | \text{AgBr(s)} | \text{Ag}$ , Calculate the EMF generated and assign correct polarity to each electrode for a spontaneous process after taking into account the cell reaction at  $25^\circ\text{C}$ . [ $K_{\text{sp}}(\text{AgCl}) = 2.8 \times 10^{-10}$ ;  $K_{\text{sp}}(\text{AgBr}) = 3.3 \times 10^{-13}$ ]

Ans.  $-0.037\text{V}$

2. Voltage of the cell  $\text{Pt}, \text{H}_2 (1\text{atm}) | \text{HOCN} (1.3 \times 10^{-3}\text{M}) || \text{Ag}^+ (0.8\text{M}) | \text{Ag(s)}$  is  $0.982\text{V}$ . Calculate the  $K_a$  for  $\text{HOCN}$ . Neglect  $[\text{H}^+]$  because of oxidation of  $\text{H}_2(\text{g})$ .

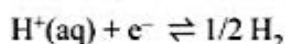


Ans.  $K_a = 6.99 \times 10^{-4}$



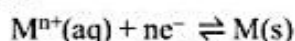
## DIFFERENT TYPES OF HALF-CELLS AND THEIR REDUCTION POTENTIAL

- (1) **Gas-Ion Half Cell** : In such a half cell, an inert collector of electrons, platinum or graphite is in contact with gas and a solution containing a specified ion. One of the most important gas-ion half cell is the hydrogen-gas-hydrogen ion half cell. In this half cell, purified  $H_2$  gas at a constant pressure is passed over a platinum electrode which is in contact with an acid solution.



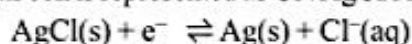
$$E_{H^+/H_2} = E_{H^+/H_2}^0 - \frac{0.0591}{1} \log \frac{(pH_2)^{1/2}}{[H^+]}$$

- (2) **Metal-Metal Ion Half Cell** : This type of cell consist of a metal M in contact with a solution containing  $M^{n+}$  ions.



$$E_{M^{n+}/M} = E_{M^{n+}/M}^0 - \frac{0.0591}{n} \log \frac{1}{[M^{n+}]}$$

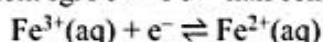
- (3) **Metal-Insoluble Salt - Anion Half Cell** : In this half cell, a metal coated with its insoluble salt is in contact with a solution containing the anion of the insoluble salt. eg. Silver-Silver Chloride Half Cell: This half cell is represented as  $Cl^-/AgCl/Ag$ . The equilibrium reaction that occurs at the electrode is



$$E_{Cl^-/AgCl/Ag} = E_{Cl^-/AgCl/Ag}^0 - \frac{0.0591}{1} \log [Cl^-]$$

potential of such cells depends upon the concentration of anions. Such cells can be used as **Reference Electrode**.

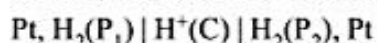
- (4) **Oxidation-reduction Half Cell**: This type of half cell is made by using an inert metal collector, usually platinum, immersed in a solution which contains two ions of the same element in different states of oxidation. eg.  $Fe^{2+} - Fe^{3+}$  half cell.



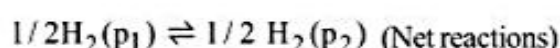
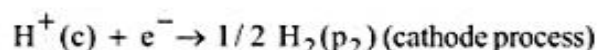
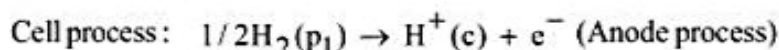
$$E_{Fe^{3+}/Fe^{2+}} = E_{Fe^{3+}/Fe^{2+}}^0 - \frac{0.0591}{1} \log \frac{[Fe^{2+}]}{[Fe^{3+}]}$$

## CONCENTRATION CELL

The cells in which electrical current is produced due to transport of a substance from higher to lower concentration. Concentration gradient may arise either in electrode material or in electrolyte. Thus there are two types of concentration cell. For such cell,  $E_{cell}^0 = 0$ .

**(i) Electrode Gas concentration cell :**

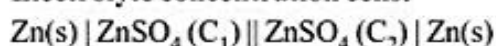
Here, hydrogen gas is bubbled at two different partial pressures at electrode dipped in the solution of same electrolyte.



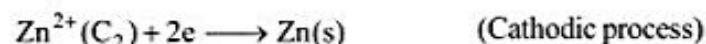
$$\therefore E = -\frac{2.303RT}{F} \log \left[ \frac{\text{p}_2}{\text{p}_1} \right]^{1/2}$$

$$\text{or At } 25^\circ\text{C, } E = \frac{0.0591}{2} \log \left[ \frac{\text{p}_1}{\text{p}_2} \right]$$

For spontaneity of such cell reaction,  $\text{p}_1 > \text{p}_2$

**(ii) Electrolyte concentration cells:**

In such cells, concentration gradient arise in electrolyte solutions. Cell process may be given as,



$\therefore$  From Nernst equation, we have

$$E = \frac{2.303RT}{2F} \log \left[ \frac{\text{C}_2}{\text{C}_1} \right]$$

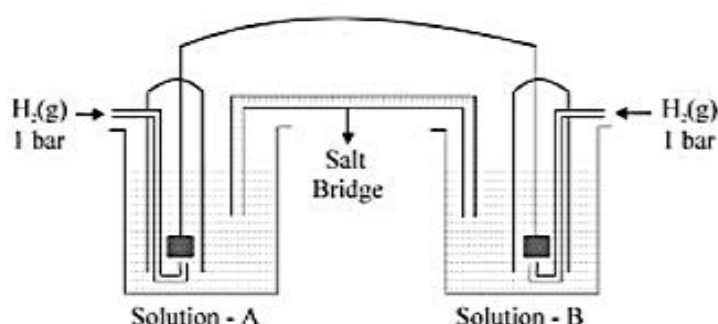
For spontaneity of such cell reaction,  $\text{C}_2 > \text{C}_1$

**Can you Explain Why ?**

- (i) Like other thermodynamic properties,  $\Delta H$ ,  $\Delta S$  and  $\Delta G$ , the sign of  $E^\circ$  changes but the magnitude of  $E^\circ$  remains the same when we reverse the cell reaction.
- (ii) Changing the stoichiometric coefficients of a half-cell reaction does not affect the value of  $E^\circ$ .

## Illustration

1. Carefully observe the given figure and using data provided find the EMF of shown Galvanic cell (in volt) :



Solution A is 0.1 M each in  $\text{NH}_4\text{OH}$  and  $\text{NH}_4\text{Cl}$  and solution B is 0.1 M  $\text{CH}_3\text{COONa}$ .

[Given :  $K_a(\text{CH}_3\text{COOH}) = 10^{-5}$ ,  $K_b(\text{NH}_4\text{OH}) = 10^{-5}$  and  $\frac{2.303RT}{F} = 0.06 \text{ volt}$ ]

- (A) 0.24 V      (B) 0.12 V      (C) 0.06 V      (D) 0 V

Ans. (D)

Sol. pH of solution (A) : Solution A is a basic Buffer

$$\text{pOH} = \text{p}K_b + \log \frac{[\text{Salt}]}{[\text{Base}]} \Rightarrow \text{pOH} = 5$$

$$\Rightarrow \text{pH} = 9 \Rightarrow [\text{H}^+]_A = 10^{-9} \text{ M}$$

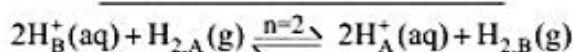
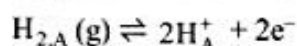
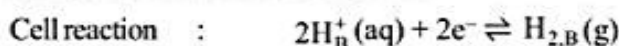
pH of solution (B)

$$\text{pH} = \frac{1}{2} [\text{p}K_w + \text{p}K_a + \log C] \Rightarrow \frac{1}{2} [14 + 5 - 1]$$

$$\text{pH} \Rightarrow 9$$

$$\Rightarrow [\text{H}^+]_B = 10^{-9}$$

Now, The cell is a concentration cell



Nearest Equation for cell

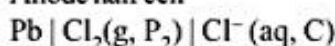
$$E_{\text{Cell}} = 0 - \frac{0.06}{2} \log \frac{[\text{H}^+]_A^2}{[\text{H}^+]_B^2} \Rightarrow 0 \text{ Volt Ans.}]$$

2.  $\text{Pt} | \text{Cl}_2(\text{g}, P_2) | \text{Cl}^-(\text{aq}, C) \parallel \text{Cl}^-(\text{aq}, C) | \text{Cl}_2(\text{g}, P_1) | \text{Pt}$   
EMF of cell is positive if

- (A)  $P_1 > P_2$       (B)  $P_2 > P_1$       (C)  $P_1 = P_2$       (D) We cannot predict

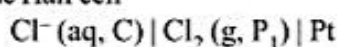
Ans. (A)

[Sol. Anode half cell



$$E_{\text{ox}} = E_{\text{ox}}^{\circ} - \frac{0.0591}{2} \log \frac{P_2}{C} \quad \dots(i)$$

Cathode Half cell



$$E_{\text{red}} = E_{\text{red}}^{\circ} - \frac{0.0591}{2} \log \frac{C}{P_1} \quad \dots(ii)$$

$$E_{\text{cell}} = E_{\text{ox}} + E_{\text{red}}$$

$$= E_{\text{ox}}^{\circ} + E_{\text{red}}^{\circ} - \frac{0.0591}{2} \log \frac{P_2}{C} \cdot \frac{C}{P_1}$$

$$E_{\text{cell}} = \frac{0.0591}{2} \log \frac{P_1}{P_2}$$

for spontaneous reaction

$$P_1 > P_2 \quad \text{Ans. (A) } ]$$

3. Calculate the standard e.m.f. of the reaction  $\text{Fe}^{3+} + 3\text{e}^{-} \rightarrow \text{Fe}_{(\text{s})}$   $E_3^{\circ} = ?$

$$\text{Given } \text{Fe}^{3+} + \text{e}^{-} \rightarrow \text{Fe}^{2+} \quad E_1^{\circ} = 0.771\text{V} \quad \text{Fe}^{2+} + 2\text{e}^{-} \rightarrow \text{Fe}_{(\text{s})} \quad E_2^{\circ} = -0.44\text{V}$$

Sol. With the help of calculation of free energy

$$\Delta G_1^{\circ} = -nFE^{\circ} = -(1)(F)(0.771\text{V}) = -0.771F$$

$$\Delta G_2^{\circ} = -(2)(F)(0.44) = 0.88F$$

$$\Delta G_3^{\circ} = -(3)(F)(E^{\circ}) = -3FE^{\circ}$$

The free energy change for the unknown process can be obtained as

$$\Delta G_3^{\circ} = \Delta G_1^{\circ} + \Delta G_2^{\circ}$$

$$-3FE^{\circ} = -0.771F + 0.88F = 0.109F$$

$$\text{or } E^{\circ} = -\frac{0.109}{3} = -0.036\text{V}$$

4. The standard electrode potentials of the electrode  $\text{Cu}^{2+}|\text{Cu}$  and  $\text{Ag}^{+}|\text{Ag}$  are 0.34V and 0.7991V respectively. What would be the concentration of  $\text{Ag}^{+}$  in a solution containing 0.06M of  $\text{Cu}^{2+}$  ion such that both the metals can be deposited together. Assume that activity coefficients are unity and both silver and copper do not dissolve among themselves.

Sol. The individual reactions are :



The electrode potentials given by Nernst equation

$$E(\text{Cu}^{2+} | \text{Cu}) = E^{\circ} = \frac{0.0591}{2} \log \frac{1}{[\text{Cu}^{2+}]} = 0.037 - \frac{(0.0591)}{2} \log \frac{1}{0.06} = 0.037 - 0.036 = 0.301$$

$$E(\text{Ag}^{+} | \text{Ag}) = 0.7991 - \frac{0.0591}{1} \log \frac{1}{[\text{Ag}^{+}]}$$

Two metals will be deposited together when the electrode potentials are equal i.e.

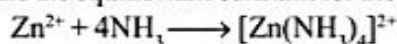
$$0.301 = 0.7991 - 0.0591 \log \frac{1}{[\text{Ag}^{+}]} \quad \text{i.e. } \log \frac{1}{[\text{Ag}^{+}]} = \frac{0.7991 - 0.301}{0.0591} = 8.428$$



$$\frac{1}{[\text{Ag}^+]} = 10^{8.428}$$

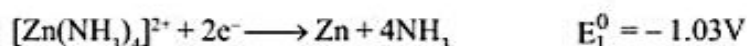
$$\text{or } [\text{Ag}^+] = 10^{-8.428} = 0.37 \times 10^{-8} \text{ mol dm}^{-3}$$

5. Calculate the equilibrium constant for the reaction,

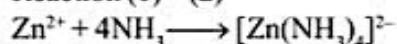


$$E^0(\text{Zn}^{2+}/\text{Zn}) = -0.763 \text{ and } E^0[\text{Zn}(\text{NH}_3)_4]^{2+}/(\text{Zn} + \text{NH}_3) = 1.03 \text{ V}$$

**Sol.** The electrode reactions for the given electrodes, can be written as



Reaction (1) – (2)



$$\text{The standard emf of this reaction} = E_1^0 - E_2^0 = -0.763 \text{ V} - (-1.03) = 0.267 \text{ V}$$

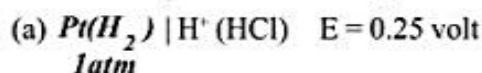
$$\text{According to Nernst equation } E = E^0 - \frac{RT}{2F} \ln \frac{a_{[\text{Zn}(\text{NH}_3)_4]^{2+}}}{a_{\text{Zn}^{2+}} \cdot a}$$

$$\text{If the process is equilibrium, } E = 0 \text{ at } 25^\circ\text{C} \quad \frac{0.0591}{2} \log K = 0.267$$

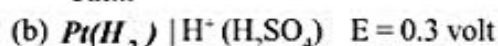
$$\log K = \frac{(0.267)(2)}{(0.059)} = 9.036 \Rightarrow K = 10^{-0.36} 10^9 = 1.09 \times 10^9$$

The equilibrium constant is also called the “Stability Constant” of the complex. If the reaction is written in a reverse manner, it will be “instability constant”.

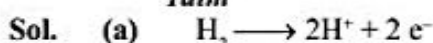
6. Calculate the pH of the following half cells solutions.



1 atm



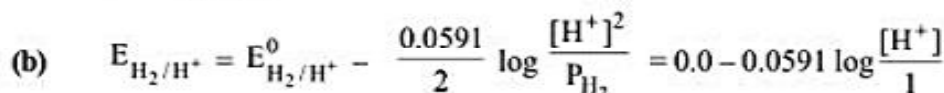
1 atm



$$E_{\text{H}_2/\text{H}^+} = E_{\text{H}_2/\text{H}^+}^0 - \frac{0.0591}{2} \log \frac{[\text{H}^+]^2}{P_{\text{H}_2}} = 0.0 - 0.0591 \log \frac{[\text{H}^+]}{1}$$

$$0.25 = 0.0591 \text{ pH}$$

$$\text{pH} = \frac{0.25}{0.0591} = 4.23$$

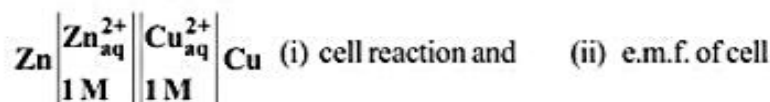


$$0.3 = 0.0591 \text{ pH}$$

$$\text{pH} = \frac{0.3}{0.591} = 5.076$$

### Exercise

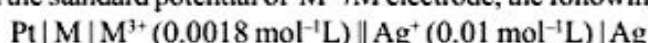
1. Calculate the values for cell



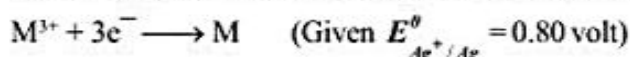
**Given :**  $E^\circ_{\text{Cu}^{2+}/\text{Cu}} = +0.35\text{V}$ ;  $E^\circ_{\text{Zn}^{2+}/\text{Zn}} = -0.76\text{V}$

- Sol.** (i) Cell reaction  $\text{Zn} + \text{Cu}^{2+} \longrightarrow \text{Zn}^{2+} + \text{Cu}$   
 (ii) 1.11 V

2. To find the standard potential of  $\text{M}^{3+}/\text{M}$  electrode, the following cell is constituted.

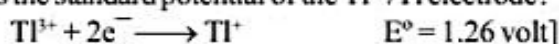


The emf of this cell is found to be 0.42 volt. Calculate the standard potential of the half reaction ,



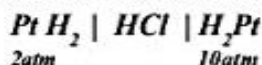
**Ans.** 0.32 volt

3. What is the standard potential of the  $\text{Tl}^{3+}/\text{Tl}$  electrode?



**Ans.** 0.728 volt

4. Calculate the emf of the following cell at  $25^\circ\text{C}$ .



**Ans.** - 0.0206 volt

5. Calculate the emf of the cell  $\text{Zn-Hg} (C_1)/\text{Zn}^{2+} (\text{aq}) | \text{Zn-Hg} (C_2)$  at  $25^\circ\text{C}$ , if the concentration of the zinc amalgam are  $C_1 = 2 \text{ gm per } 100 \text{ gm of Hg}$  and  $C_2 = 1 \text{ gm per } 100 \text{ gm of Hg}$ .

**Ans.**  $8.8 \times 10^{-3}\text{V}$

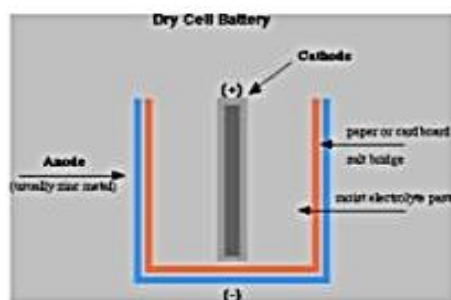
## COMMERCIAL VOLTAIC CELLS

Batteries can be classified as primary and secondary. Primary batteries can not be returned to their original state by recharging, so when the reactants are consumed, the battery is "dead" and must be discarded. Secondary batteries are often called storage batteries or rechargeable batteries. The reactions in these batteries can be reversed; thus, the batteries can be recharged.

### PRIMARY BATTERIES

#### Dry cells and alkaline batteries

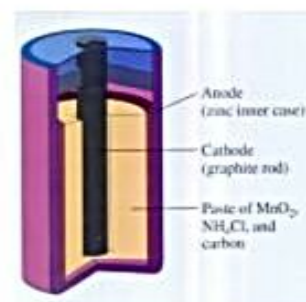
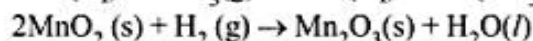
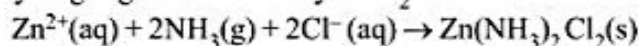
Zinc serves as the anode, and the cathode is a graphite rod placed down the center of the device. These cells are often called "dry cells" because there is no visible liquid phase. However, water is present, so the cell contains a moist paste of  $\text{NH}_4\text{Cl}$ ,  $\text{ZnCl}_2$  and  $\text{MnO}_2$ . The moisture is necessary because the ions present must be in a medium in which they can migrate from one electrode to the other. The cell generates a potential of 1.5 V using the following half-reactions:



Cathode, reductions:  $2\text{NH}_4^+(\text{aq}) + 2\text{e}^- \rightarrow 2\text{NH}_3(\text{g}) + \text{H}_2(\text{g})$

Anode, Oxidation:  $\text{Zn}(\text{s}) \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}^-$

The two gases formed at the cathode will build up pressure and could cause the cell to rupture. This problem is avoided, however, by two other reactions that take place in the cell. Ammonia molecules bind to  $\text{Zn}^{2+}$  ions, and hydrogen gas is oxidized by  $\text{MnO}_2$  to water.



LeClanche cells were widely used because of their low cost, but they have several disadvantages. If current is drawn from the battery rapidly, the gaseous products cannot be consumed rapidly enough, so the cell resistance rises, and the voltage drops. In addition, the zinc electrode and ammonium ions are in contact in the cell, and these chemicals react slowly. Recall that zinc reacts with acid to form hydrogen. The ammonium ion,  $\text{NH}_4^+(\text{aq})$ , is a weak Bronsted acid and reacts slowly with zinc. Because of this reaction, these voltaic cells cannot be stored indefinitely. When the zinc outer shell deteriorates, the battery can leak acid and perhaps damage the appliance in which it is contained.

At the present time **alkaline batteries** are used the chemistry of alkaline cells is quite similar to that in a LeClanche cell, except that the material inside the cell is basic (alkaline). Alkaline cells use the oxidation of zinc and the reduction of  $\text{MnO}_2$  to generate a current, but  $\text{NaOH}$  or  $\text{KOH}$  is used in the cell instead of the acidic salt  $\text{NH}_4\text{Cl}$ .

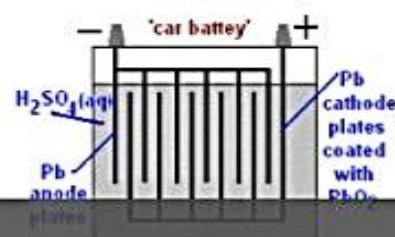
Cathode, reductions:  $2\text{MnO}_2(\text{s}) + \text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightarrow \text{Mn}_2\text{O}_3(\text{s}) + 2\text{OH}^-(\text{aq})$

Anode, Oxidation:  $\text{Zn}(\text{s}) + 2\text{OH}^-(\text{aq}) \rightarrow \text{ZnO}(\text{s}) + \text{H}_2\text{O}(\text{l}) + 2\text{e}^-$

Alkaline cells, which produce 1.54 V (approximately the same voltage as the LeClanche cell), have the further advantage that the cell potential does not decline under high current loads because no gases are formed.

## SECONDARY OR RECHARGEABLE BATTERIES

An automobile battery – the **lead storage battery** – is probably the best-known rechargeable battery figure. The 12-V version of this battery contains six voltaic cells, each generating about 2V. The lead storage battery can produce a large initial current, an essential feature when starting an automobile engine.





When the cell supplies electrical energy, the lead anode is oxidized to lead (II) sulfate, an insoluble substance that adheres to the electrode surface. The two electrons produced per lead atom move through the external circuit to the cathode, where  $\text{PbO}_2$  is reduced to  $\text{Pb}^{2+}$  ions that, in the presence of  $\text{H}_2\text{SO}_4$ , also form lead (II) sulfate.

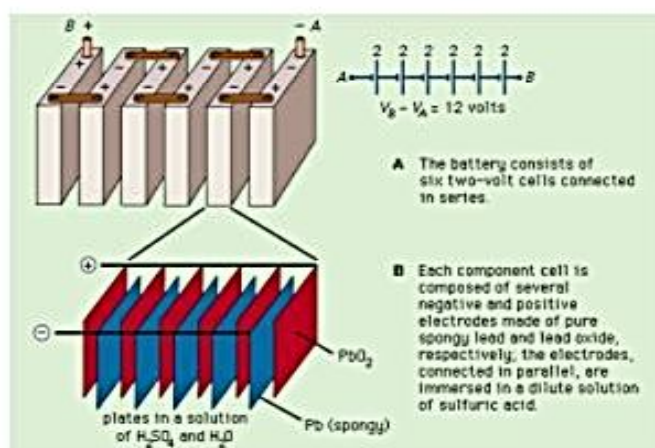
Cathode, reduction :  $\text{PbO}_2(\text{s}) + 4\text{H}^+(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) + 2\text{e}^- \rightarrow \text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O}(\text{l})$

Anode, oxidation :  $\text{Pb}(\text{s}) + \text{SO}_4^{2-}(\text{aq}) \rightarrow \text{PbSO}_4(\text{s}) + 2\text{e}^-$

Net cell reaction  $\text{Pb}(\text{s}) + \text{PbO}_2(\text{s}) + 2\text{H}_2\text{SO}_4(\text{aq}) \rightarrow 2\text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O}(\text{l})$



The discharging process of the storage cell is based on the principles of electrochemical cell, whereas the charging process is based upon the principles of electrolytic cells.



**Nickel - Cadmium ("Ni - Cad") batteries**, used in variety of cordless appliances such as telephones, video camcorders, and cordless power tools, are lightweight and rechargeable. The chemistry of the cell utilizes the oxidation of cadmium and the reduction of nickel (III) oxide under basic conditions.

Cathode, reduction :  $\text{NiO}(\text{OH})(\text{s}) + \text{H}_2\text{O}(\text{l}) + \text{e}^- \rightarrow \text{Ni}(\text{OH})_2(\text{s}) + \text{OH}^-(\text{aq}) / \times 2$

Anode, Oxidation:  $\text{Cd}(\text{s}) + 2\text{OH}^- \rightarrow \text{Cd}(\text{OH})_2(\text{s}) + 2\text{e}^-$

Net cell reaction :  $2\text{NiO}(\text{OH})(\text{s}) + \text{Cd}(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightarrow 2\text{Ni}(\text{OH})_2(\text{s}) + \text{Cd}(\text{OH})_2(\text{s})$

As the active masses of all reaction components are independent of their amount. The cell delivers constant EMF throughout.

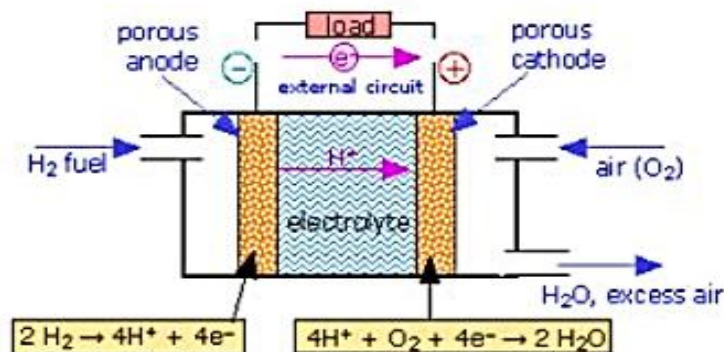
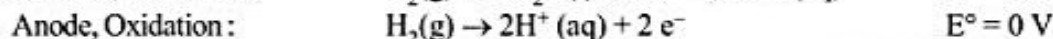
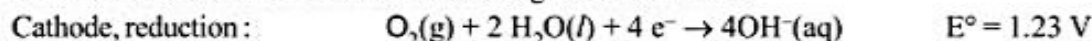
## FUEL CELLS AND HYBRID CARS

An advantage of voltaic cells is that they are small and portable, but their size is also a limitation. The amount of electric current produced is limited by the quantity of reagents contained in the cell. When one of the reactants is completely consumed, the cell will no longer generate a current. Fuel cells avoid this limitation because the reactants (fuel and oxidant) can be supplied continuously to the cell from an external reservoir.

In a Hydrogen - Oxygen fuel cell figure, hydrogen is pumped into the anode of the cell, and  $\text{O}_2$  (or air)



is directed to the cathode where the following reactions occur :



Schematic diagram of a modern hydrogen-oxygen fuel cell.

Commonly used electrolytes are NaOH solution, phosphoric acid, or solid oxides. A major limitation of any oxygen-consuming fuel cell is the slow rate of the reduction of this element at a cathode. The best cathode surfaces are usually made of platinum, which is a major cost factor in fuel cell design.

## EFFICIENCY OF A FUEL CELL

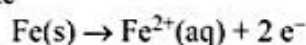
$$\eta = \frac{(\Delta G)}{(\Delta H)} \times 100$$

## CORROSION CELLS AND REACTIONS

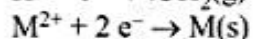
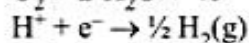
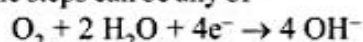
Corrosion can be defined as the deterioration of materials by chemical processes. Of these, the most important by far is electrochemical corrosion of metals, in which the oxidation process  $\text{M} \rightarrow \text{M}^+ + \text{e}^-$  is facilitated by the presence of a suitable electron acceptor, sometimes referred to in corrosion science as a **depolarizer**.

In a sense, corrosion can be viewed as the spontaneous return of metals to their ores; the huge quantities of energy that were consumed in mining, refining, and manufacturing metals into useful objects is dissipated by a variety of different routes.

The special characteristic of most corrosion processes is that the oxidation and reduction steps occur at separate locations on the metal. This is possible because metals are conductive, so the electrons can flow through the metal from the anodic to the cathodic regions. The presence of water is necessary in order to transport ions to and from the metal, but a thin film of adsorbed moisture can be sufficient. A corrosion system can be regarded as a short-circuited electrochemical cell in which the anodic process is something like



and the cathodic steps can be any of



where M is a metal. Which parts of the metal serve as anodes and cathodes can depend on many factors, as can be seen from the irregular corrosion patterns that are commonly observed. Atoms in regions that have undergone stress, as might be produced by forming or machining, often tend to have higher free energies, and thus tend to become anodic.

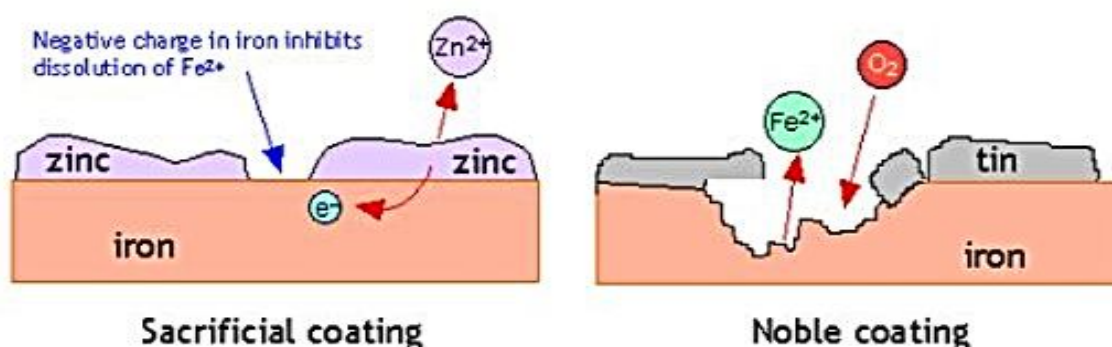
## CONTROL OF CORROSION

Since both the cathodic and anodic steps must take place for corrosion to occur, prevention of either one will stop corrosion. The most obvious strategy is to stop both processes by coating the object with a paint or other protective coating. Even if this is done, there are likely to be places where the coating is broken or does not penetrate, particularly if there are holes or screw threads.

A more sophisticated approach is to apply a slight negative charge to the metal, thus making it more difficult for the reaction  $M \rightarrow M^{2+} + 2e^-$  to take place.

## SACRIFICIAL COATINGS

One way of supplying this negative charge is to apply a coating of a more active metal. Thus a very common way of protecting steel from corrosion is to coat it with a thin layer of zinc; this process is known as galvanizing. The zinc coating, being less noble than iron, tends to corrode selectively. Dissolution of this sacrificial coating leaves behind electrons which concentrate in the iron, making it cathodic and thus inhibiting its dissolution.



The effect of plating iron with a less active metal provides an interesting contrast. The common tin-plated can (on the right) is a good example. As long as the tin coating remains intact, all is well, but exposure of even a tiny part of the underlying iron to the moist atmosphere initiates corrosion. The electrons released from the iron flow into the tin, making the iron more anodic so now the tin is actively promoting corrosion of the iron! You have probably observed how tin cans disintegrate very rapidly when left outdoors.

## CATHODIC PROTECTION

A more sophisticated strategy is to maintain a continual negative electrical charge on a metal, so that its dissolution as positive ions is inhibited. Since the entire surface is forced into the cathodic condition, this method is known as cathodic protection. The source of electrons can be an external direct current power supply (commonly used to protect oil pipelines and other buried structures), or it can be the corrosion of another, more active metal such as a piece of zinc or aluminum buried in the ground nearby.

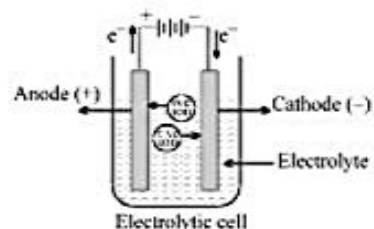


## ELECTROLYSIS

The decomposition of electrolyte solution by passage of electric current, resulting into deposition of metals or liberation of gases at electrodes is known as electrolysis.

### ELECTROLYTIC CELL

This cell converts electrical energy into chemical energy. The entire assembly except that of the external battery is known as the electrolytic cell



### ELECTRODES

The metal strip at which positive current enters is called **anode**; anode is positively charged in electrolytic cell. On the other hand, the electrode at which current leaves is called **cathode**. Cathodes are negatively charged.

Anode	Positive	Loss of electron or oxidation takes place	Positive current enters
Cathode	Negative	Gain of electron or reduction takes place	Current leaves

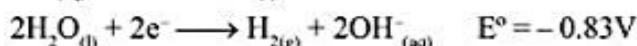
### ELECTROLYSIS OF MOLTEN SODIUM CHLORIDE

Reactions at	$\text{NaCl}(\text{molten}) \longrightarrow \text{Na}^+ + \text{Cl}^-$		
	anode (oxidation)	:	cathode (reduction)
	$2\text{Cl}^- \longrightarrow \text{Cl}_2(\text{g}) + 2\text{e}^-$		$2\text{Na}^+ + 2\text{e}^- \longrightarrow 2\text{Na}(\text{l})$

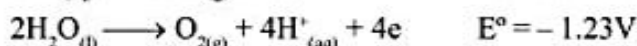
There are two types of electrodes used in the electrolytic cell, namely attackable and non - attackable. The attackable electrodes participate in the electrode reaction. They are made up of reactive metals like Zn, Cu, Ag etc. In such electrodes, atom of the metal gets oxidised into the corresponding cation, which is passed into the solution. Thus, such anodes get dissolved and their mass decreases. On the other hand, non-attackable electrodes do not participate in the electrode reaction as they are made up of unreactive elements like Pt, graphite etc. Such electrodes do not dissolve and their mass remains the same.

### ELECTROLYSIS OF SODIUM CHLORIDE SOLUTIONS

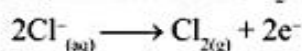
When you electrolyze an aqueous solution of sodium chloride, NaCl, the possible species involved in half-reactions are  $\text{Na}^+$ ,  $\text{Cl}^-$  and  $\text{H}_2\text{O}$ . The possible cathode half-reactions are



Under standard conditions, you expect  $\text{H}_2\text{O}$  to be reduced in preference to  $\text{Na}^+$ , which agrees with what you observe. Hydrogen is evolved at the cathode.

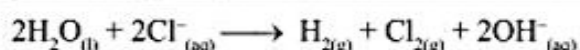
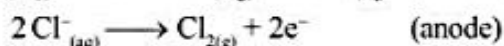
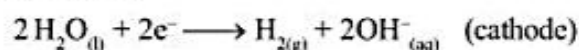


Under standard-state conditions, you might expect  $\text{H}_2\text{O}$  to be oxidized in preference to  $\text{Cl}^-$ . However, the potentials are close and over voltages at the electrodes could alter this conclusion. It is possible nevertheless to give a general statement about the product expected at the anode. Electrode potentials, as you have seen, depend on concentrations. It turns out that when the solution is concentrated enough in  $\text{Cl}^-$ ,  $\text{Cl}_2$  is the product; but in dilute solution,  $\text{O}_2$  is the product. To see this, you would simply apply the Nernst equation of the  $\text{Cl}^-|\text{Cl}_2$  half reaction.



Starting with very dilute  $\text{NaCl}$  solutions, you would find that the oxidation potential of  $\text{Cl}^-$  is very negative, so  $\text{H}_2\text{O}$  is reduced in preference to  $\text{Cl}^-$ . But as you increase the  $\text{NaCl}$  concentration, you would find that the oxidation potential of  $\text{Cl}^-$  increases until eventually  $\text{Cl}^-$  is oxidized in preference to  $\text{H}_2\text{O}$ . The product changes from  $\text{O}_2$  to  $\text{Cl}_2$ .

The half-reactions and cell reaction for the electrolysis of aqueous sodium chloride to chlorine and hydroxide ion are as follows:



Because the electrolysis started with sodium chloride, the cation in the electrolyte solution is  $\text{Na}^+$ . When you evaporate the electrolyte solution at the cathode, you obtain sodium hydroxide  $\text{NaOH}$ .

## QUALITATIVE ASPECTS OF ELECTROLYSIS

- (i) Of the two cations, that cation is liberated at the cathode which has higher reduction potential. Of the two anions, that anion will be discharged at the anode which has lower reduction potential.
- (ii) If electrode is active at cathode, metal goes on depositing on cathode and at anode metal is dissolved.
- (iii) It must be noted that it is not the SRP of a cation that decides its discharge, but its reduction potential. The SRP's should be used only when the concentration of ions are 1M. For concentrations other than 1M, the reduction potentials for each cation at the concentration is calculated and then the discharge of an ion can be predicted.
- (iv) The discharge of  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$  and  $\text{SO}_4^{2-}$  ions at anode does not commonly take place from aqueous solution.





Electrolysis of water is often done with a small amount of sulphuric acid added to water. Why?

## FARADAY'S LAWS OF ELECTROLYSIS

### (i) *First law of electrolysis :*

Amount of substance deposited or liberated at an electrode is directly proportional to amount of charge passed (utilized) through the solution.

$$w \propto Q$$

$W$  = weight liberated,  $Q$  = charge in coulomb

$$w = ZQ$$

$Z$  = electrochemical equivalent

when  $Q = 1$  coulomb, then  $w = Z$

Thus, weight deposited by 1 coulomb charge is called **electrochemical equivalent**.

Let 1 ampere current is passed till ' $t$ ' seconds .

Then,  $Q = It$   $\therefore w = ZIt$

1 Faraday = 96500 coulomb = Charge of one mole electrons

***One faraday is the charge required to liberate or deposit one gm equivalent of a substance at corresponding electrode.***

Let ' $E$ ' is equivalent weight then ' $E$ ' gm will be liberated by 96500 coulomb.

$\therefore$  1 Coulomb will liberate  $\frac{E}{96500}$  gm ; By definition,  $Z = \frac{E}{96500}$

$$\therefore W = \frac{ItE}{96500}$$

When a gas is evolved at an electrode, then above formula changes as,

$$V = \frac{ItV_e}{96500}$$

where  $V$  = volume of liberated gas,  $V_e$  = equivalent volume of gas.

Equivalent volume may be defined as:

The volume of gas liberated by 96500 coulomb at 1atm & 0°C.

### (ii) *Second law of electrolysis :*

When same amount of charge is passed through different electrolyte solutions connected in series then weight of substances deposited or dissolved at anode or cathode are in ratio of their equivalent weights. i.e.

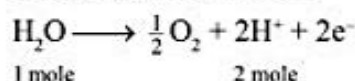
$$w_1/w_2 = E_1/E_2$$

**Illustration**

1 How much electric charge is required to oxidise :

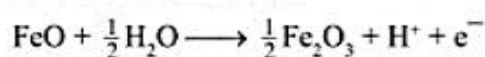
- (a) 1 mole of  $\text{H}_2\text{O}$  to  $\text{O}_2$  (b) 1 mole of  $\text{FeO}$  to  $\text{Fe}_2\text{O}_3$ ?

Sol. (a) The oxidation reaction is :



$$Q = 2F = 2 \times 96500 = 1.93 \times 10^5 \text{ C}$$

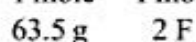
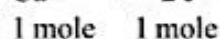
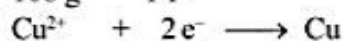
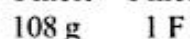
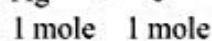
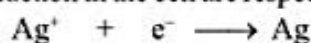
(b) The oxidation reaction is



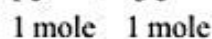
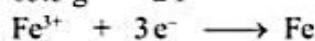
$$Q = F = 96500 \text{ coulomb}$$

2. Exactly 0.4 faraday electric charge is passed through three electrolytic cells in series, first containing  $\text{AgNO}_3$ , second  $\text{CuSO}_4$  and third  $\text{FeCl}_3$  solution. How many gram of each metal will be deposited assuming only cathodic reaction in each cell.

Sol. The cathodic reaction in the cell are respectively,



and



Hence,

$$\text{Ag deposited} = 108 \times 0.4 = 43.2 \text{ g}$$

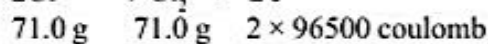
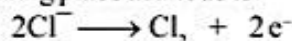
$$\text{Cu deposited} = \frac{63.5}{2} \times 0.4 = 12.7 \text{ g}$$

and

$$\text{Fe deposited} = \frac{56}{3} \times 0.4 = 7.47 \text{ g}$$

3. An electric current of 100 ampere is passed through a molten liquid of sodium chloride for 5 hours. Calculate the volume of chlorine gas liberated at the electrode at NTP.

Sol. The reaction taking place at anode is



$$Q = i \times t = 100 \times 5 \times 60 \times 60 \text{ coulomb}$$

The amount of chlorine liberated by passing  $100 \times 5 \times 60 \times 60$  coulomb of electric charge.

$$= \frac{1}{2 \times 96500} \times 100 \times 5 \times 60 \times 60 = 9.3264 \text{ mole}$$

$$\text{Volume of } \text{Cl}_2 \text{ liberated at NTP} = 9.3264 \times 22.4 = 208.91 \text{ L}$$

4. How long a current of 2A has to be passed through a solution of  $\text{AgNO}_3$  to coat a metal surface of  $80\text{cm}^2$  with  $5\mu\text{m}$  thick layer? Density of silver =  $10.8\text{g/cm}^3$ .

Ans.  $t = 193 \text{ sec}$

Sol.  $I = \frac{M}{V} \Rightarrow 10.8 = \frac{M}{80 \times 5 \times 10^{-4}} \Rightarrow M = 10.8 \times 400 \times 10^{-4}$

$$M = 43.2 \times 10^{-2} \text{ gm}$$

$$\text{Eq. of Ag} = \frac{It}{96500}$$

$$\frac{43.2 \times 10^{-2}}{108} = \frac{2 \times t}{96500} = t = 193 \text{ sec}$$

### Exercise

1. What current strength in ampere will be required to liberate 10 g of chlorine from sodium chloride solution in one hour?

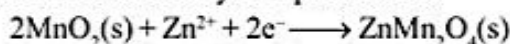
Ans. 7.55 ampere

2. A current of 2.68 ampere is passed for one hour through an aqueous solution of copper sulphate using copper electrodes. Calculate the change in mass of cathode and that of the anode. (at. mass of copper = 63.5).

Ans. 3.174 g

3. In a zinc manganese dioxide dry cell, the anode is made up of zinc and cathode of a carbon rod surrounded by a mixture of  $\text{MnO}_2$ , carbon,  $\text{NH}_4\text{Cl}$  and  $\text{ZnCl}_2$  in aqueous base.

The cathodic reaction may be represented as



Let there be 8 g  $\text{MnO}_2$  in the cathodic compartment. How many days will the dry cell continue to give a current of  $4 \times 10^{-3}$  ampere.

Ans. 25.675 day

## CONDUCTANCE

### Introduction

Both metallic and electrolytic conductors obey Ohm's law

i.e.  $V = IR$

where  $V$  = Potential difference in volt;  $I$  = Current in ampere ;  $R$  = resistance in Ohm

We know, resistance is directly proportional to length of conductor and inversely proportional to cross sectional area of the conductor.

$$R \propto \frac{l}{A} \quad \text{or} \quad R = \rho \frac{l}{A} \quad (\rho = \text{Specific resistance})$$

Specific resistance is the resistance of a conductor having lengths of 1 cm and cross sectional area of 1 cm<sup>2</sup>.

Unit of R is ohm and unit of specific resistance is ohm cm

Reciprocal of resistance is called as *conductance* and reciprocal of specific resistance is called as *specific conductance*.

$$\frac{1}{R} = \frac{1}{\rho l} \quad \text{or} \quad C = K \frac{A}{l}$$

where C = conductance ohm<sup>-1</sup>; K = specific conductance ohm<sup>-1</sup>cm<sup>-1</sup>.

Mho and siemens are other units of conductance

$$K = \frac{l}{A} C$$

Specific conductance = Cell constant × Conductance

$$k = G^* \times G$$

### SPECIFIC CONDUCTANCE IS CONDUCTANCE OF 1 CM<sup>3</sup> OF AN ELECTROLYTE SOLUTION

In case of electrolytic solution, the specific conductance is defined as the conductance of a solution of definite concentration enclosed in a cell having two electrodes of unit area separated by 1 cm apart.

#### 1. Equivalent Conductance

Equivalent conductance is the conductance of an electrolyte solution containing 1 gm equivalent of electrolyte. It is denoted by  $\wedge$ .

$$\wedge = K \times V$$

$$(\wedge = \text{ohm}^{-1} \text{cm}^{-1} \times \text{cm}^3 = \text{ohm}^{-1} \text{cm}^2)$$

Usually concentration of electrolyte solution is expressed as C gm equivalent per litre.

$$\text{Thus, } V = \frac{1000}{C}$$

$$\{\text{Volume having 1 gm equivalent electrolyte in the solution}\} \text{ Thus, } \wedge = K \times \frac{1000}{C}$$

#### 2. Molar Conductance

Molar conductance may be defined as conductance of an electrolyte solution having 1 gm mole electrolyte in a litre. It is denoted by  $\wedge_m$ .

$$\wedge_m = K \times V$$

Usually concentration of electrolyte solution is expressed as 'M' gm mole electrolyte per litre.

$$\text{Thus, } V = \frac{1000}{M}$$

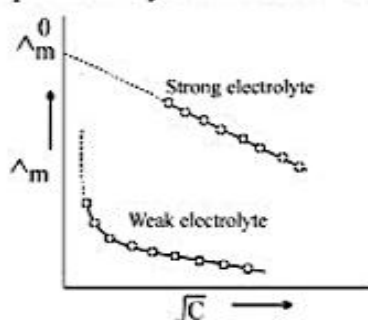
$$\text{Hence, } \wedge_m = K \times \frac{1000}{M}$$

$$\text{Relation between } \wedge \text{ and } \wedge_m : \quad \wedge_m = n \times \wedge$$



### DETERMINATION OF $\Lambda_m^0$ OR $\Lambda^0$

A plot of  $\Lambda_m$  vs  $\sqrt{C}$  as found experimentally is as shown below graphically.



The  $\Lambda_m$  vs  $\sqrt{C}$  plot of strong electrolyte being linear it can be extrapolated to zero concentration. Thus,  $\Lambda_m$  values of the solution of the test electrolyte are determined at various concentrations the concentrations should be as low as good.

$\Lambda_m$  values are then plotted against  $\sqrt{C}$  when a straight line is obtained. This is the extrapolated to zero concentration. The point where the straight line intersects  $\Lambda_m$  axis is  $\Lambda_m^0$  of the strong electrolyte.

However, the plot in the case weak electrolyte being non linear, shooting up suddenly at some low concentration and assuming the shape of a straight line parallel to  $\Lambda_m$  axis. Hence extrapolation in this case is not possible. Thus,  $\Lambda_0$  of a weak electrolyte cannot be determined experimentally. It can, however, be done with the help of Kohlrausch's law to be discussed later.



**Is electrolytic conductance depends on temperature ?**

#### Kohlrausch's Law of Independent Migration of Ions

Kohlrausch determined  $\Lambda_0$  values of pairs of some strong electrolytes containing same cation say KF and KCl, NaF and NaCl etc., and found that the difference in  $\Lambda_0$  values in each case remains the same:

$$\Lambda_m^0(\text{KCl}) - \Lambda_m^0(\text{KF}) = \Lambda_m^0(\text{NaCl}) - \Lambda_m^0(\text{NaF})$$

He also determined  $\Lambda_0$  values of pairs of strong electrolytes containing same anion say KF and NaF, KCl and NaCl etc. and found that the difference in  $\Lambda_0$  values in each case remains the same.

$$\Lambda_m^0(\text{KF}) - \Lambda_m^0(\text{NaF}) = \Lambda_m^0(\text{KCl}) - \Lambda_m^0(\text{NaCl})$$

This experimental data led him to formulate the following law called Kohlrausch's law of independent migration of ions.

At infinite dilution when dissociation is complete, every ion makes some definite contribution towards molar conductance of the electrolyte irrespective of the nature of the other ion which with it is associated and that the molar conductance at infinite dilution for any electrolyte is given by the sum of the contribution of the two ions. Thus,

$$\Lambda_m^0 = \lambda_+^0 + \lambda_-^0$$

Where  $\lambda_+^0$  is the contribution of the cation and  $\lambda_-^0$  is the contribution of the anion towards the molar conductance at infinite dilution. These contributions are called molar ionic conductances at infinite dilution. Thus,  $\lambda_+^0$  is the molar ionic conductance of cation and  $\lambda_-^0$  is the molar ionic conductance of anion, at infinite dilution. The above equation is, however, correct only for binary electrolyte like NaCl,  $\text{MgSO}_4$  etc.

## APPLICATION OF KOHLRAUSCH'S LAW

### (1) Determination of $\Lambda_m^0$ of a weak electrolyte:

In order to calculate  $\Lambda_m^0$  of a weak electrolyte say  $\text{CH}_3\text{COOH}$ , we determine experimentally  $\Lambda_m^0$  values of the following three strong electrolytes:

- A strong electrolyte containing same cation as in the test electrolyte, say HCl
- A strong electrolyte containing same anion as in the test electrolyte, say  $\text{CH}_3\text{COONa}$
- A strong electrolyte containing same anion of (a) and cation of (b) i.e. NaCl.

$\Lambda_m^0$  of  $\text{CH}_3\text{COOH}$  is then given as:

$$\Lambda_m^0(\text{CH}_3\text{COOH}) = \Lambda_m^0(\text{HCl}) + \Lambda_m^0(\text{CH}_3\text{COONa}) - \Lambda_m^0(\text{NaCl})$$

Proof:

$$\Lambda_m^0(\text{HCl}) = \lambda_{\text{H}^+}^0 + \lambda_{\text{Cl}^-}^0 \quad \dots\dots\dots(\text{i})$$

$$\Lambda_m^0(\text{CH}_3\text{COONa}) = \lambda_{\text{CH}_3\text{COO}^-}^0 + \lambda_{\text{Na}^+}^0 \quad \dots\dots\dots(\text{ii})$$

$$\Lambda_m^0(\text{NaCl}) = \lambda_{\text{Na}^+}^0 + \lambda_{\text{Cl}^-}^0 \quad \dots\dots\dots(\text{iii})$$

Adding equation (i) and equation (ii) and subtracting (iii) from them:

$$\Lambda_m^0(\text{HCl}) + \Lambda_m^0(\text{CH}_3\text{COONa}) - \Lambda_m^0(\text{NaCl}) = \lambda_{\text{H}^+}^0 + \lambda_{\text{CH}_3\text{COO}^-}^0 = \Lambda_m^0(\text{CH}_3\text{COOH})$$

### (2) Determination of degree of dissociation ( $\alpha$ ):

$$\alpha = \frac{\text{No. of molecules ionised}}{\text{total number of molecules dissolved}} = \frac{\Lambda_m}{\Lambda_m^0}$$

### (3) Determination of solubility of sparingly soluble salt

The specific conductivity of a saturated solution of the test electrolyte (sparingly soluble) made in conductivity water is determined by the method as described above. From this the specific conductivity of conductivity water is deducted. The molar conductance of the saturated solution is taken to be equal to  $\Lambda_m^0$  as the saturated solution of a sparingly soluble salt is extremely dilute. Hence from equation (4).

$$\Lambda_m^0 = \frac{1000\kappa}{C},$$

where C is the molarity of solution and hence the solubility.

**Illustration**

1. 1.0 N solution of a salt surrounding two platinum electrodes 2.1 cm apart and 4.2 sq cm in area was found to offer a resistance of 50 ohm. Calculate the equivalent conductivity of the solution.

**Sol.** Given  $l = 2.1$  cm,  $a = 4.2$  sq. cm,  $R = 50$  ohm

$$\text{Specific conductance, } \kappa = \frac{l}{a} \cdot \frac{1}{R}$$

$$\text{or } \kappa = \frac{2.1}{4.2} \times \frac{1}{50} = 0.01 \text{ ohm}^{-1} \text{ cm}^{-1}$$

$$\text{Equivalent conductivity} = \kappa \times V$$

$$V = \text{the volume containing 1 g equivalent} = 1000 \text{ ml}$$

$$\text{So Equivalent conductivity} = 0.01 \times 1000 = 10 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}$$

2. The equivalent conductances of sodium chloride, hydrochloric acid and sodium acetate at infinite dilution are 126.45, 426.16 and 91.0 ohm<sup>-1</sup> cm<sup>2</sup> equiv<sup>-1</sup>, respectively at 25 °C. Calculate the equivalent conductance of acetic acid at infinite dilution.

**Sol.** According to Kohlrausch's law,

$$\Lambda_{\infty \text{CH}_3\text{COONa}} = \lambda_{\text{CH}_3\text{COO}^-} + \lambda_{\text{Na}^+} = 91.0 \quad \text{.....(i)}$$

$$\Lambda_{\infty \text{HCl}} = \lambda_{\text{H}^+} + \lambda_{\text{Cl}^-} = 426.16 \quad \text{.....(ii)}$$

$$\Lambda_{\infty \text{NaCl}} = \lambda_{\text{Na}^+} + \lambda_{\text{Cl}^-} = 126.45 \quad \text{.....(iii)}$$

Adding equations (i) and (ii) and subtracting (iii),

$$\begin{aligned} \lambda_{\text{CH}_3\text{COO}^-} + \lambda_{\text{Na}^+} + \lambda_{\text{H}^+} + \lambda_{\text{Cl}^-} - \lambda_{\text{Na}^+} - \lambda_{\text{Cl}^-} \\ = 91.0 + 426.16 - 126.45 \end{aligned}$$

$$\lambda_{\text{CH}_3\text{COO}^-} + \lambda_{\text{H}^+} = \Lambda_{\infty \text{CH}_3\text{COOH}} = 390.7 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}$$

3. The specific conductivity of a saturated solution of silver chloride is  $2.30 \times 10^{-6}$  mho cm<sup>-1</sup> at 25 °C. Calculate the solubility of silver chloride at 25 °C ;

if  $\lambda_{\text{Ag}^+} = 61.9$  mho cm<sup>2</sup> mol<sup>-1</sup> and  $\lambda_{\text{Cl}^-} = 76.3$  mho cm<sup>2</sup> mol<sup>-1</sup>.

**Sol.** Let the solubility of AgCl be  $s$  gram mole per litre

$$\text{Dilution} = \frac{1000}{s}$$

$$\Lambda_{\infty \text{AgCl}} = \lambda_{\text{Ag}^+} + \lambda_{\text{Cl}^-} = 61.9 + 76.3 = 138.2 \text{ mho cm}^2 \text{ mol}^{-1}$$

$$\text{Sp. conductivity} \times \text{dilution} = \Lambda_{\infty \text{AgCl}} = 138.2$$

$$2.30 \times 10^{-6} \times \frac{1000}{s} = 138.2$$

$$s = \frac{2.30 \times 10^{-3}}{138.2} = 1.66 \times 10^{-5} \text{ mole per litre} = 1.66 \times 10^{-5} \times 143.5 \text{ gL}^{-1} = 2.382 \times 10^{-3} \text{ gL}^{-1}$$



### Exercise

- Specific conductance of a decinormal solution of KCl is  $0.0112 \text{ ohm}^{-1} \text{ cm}^{-1}$ . The resistance of a cell containing the solution was found to be 56. What is the cell constant?  
**Ans.**  $0.6272 \text{ cm}^{-1}$
- The specific conductivity of 0.02 M KCl solution at  $25^\circ\text{C}$  is  $2.768 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$ . The resistance of this solution at  $25^\circ\text{C}$  when measured with a particular cell was 250.2 ohms. The resistance of 0.01 M  $\text{CuSO}_4$  solution at  $25^\circ\text{C}$  measured with the same cell was 8331 ohms. Calculate the molar conductivity of the copper sulphate solution.  
**Ans.**  $8.312 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$
- A 0.05 N solution of a salt occupying a volume between two platinum electrodes separated by a distance of 1.72 cm and having an area of  $4.5 \text{ cm}^2$  has a resistance of 250 ohm. Calculate the equivalent conductance of the solution.  
**Ans.**  $30.56 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$
- A decinormal solution of NaCl has specific conductivity equal to 0.0092. If ionic conductance of  $\text{Na}^+$  and  $\text{Cl}^-$  ions at the same temperature are 43.0 and  $65.0 \text{ ohm}^{-1}$  respectively, calculate the degree of dissociation of NaCl solution.  
**Ans.** 0.85

### ELECTROCHEMICAL SERIES

S.No.	Reduction half cell reaction	$E^\circ$ in volts at $25^\circ\text{C}$
1.	$\text{F}_2 + 2\text{e}^- \longrightarrow 2\text{F}^-$	+ 2.65
2.	$\text{S}_2\text{O}_8^{2-} + 2\text{e}^- \longrightarrow 2\text{SO}_4^{2-}$	+ 2.01
3.	$\text{Co}^{3+} + \text{e}^- \longrightarrow \text{Co}^{2+}$	+ 1.82
4.	$\text{PbO}_2 + 4\text{H}^+ + \text{SO}_4^{2-} + 2\text{e}^- \longrightarrow \text{PbSO}_4 + 2\text{H}_2\text{O}$	+ 1.65
5.	$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \longrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$	+ 1.52
6.	$\text{Au}^{3+} + 3\text{e}^- \longrightarrow \text{Au}$	+ 1.50
7.	$\text{Cl}_2 + 2\text{e}^- \longrightarrow 2\text{Cl}^-$	+ 1.36
8.	$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \longrightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	+ 1.33
9.	$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \longrightarrow 2\text{H}_2\text{O}$	+ 1.229
10.	$\text{Br}_2 + 2\text{e}^- \longrightarrow 2\text{Br}^-$	+ 1.07
11.	$\text{NO}_3^- + 4\text{H}^+ + 3\text{e}^- \longrightarrow \text{NO} + 2\text{H}_2\text{O}$	+ 0.96
12.	$2\text{Hg}^{2+} + 2\text{e}^- \longrightarrow \text{Hg}_2^{2+}$	+ 0.92
13.	$\text{Cu}^{2+} + \text{I}^- + \text{e}^- \longrightarrow \text{CuI}$	+ 0.86
14.	$\text{Ag}^+ + \text{e}^- \longrightarrow \text{Ag}$	+ 0.799
15.	$\text{Hg}_2^{2+} + 2\text{e}^- \longrightarrow 2 \text{Hg}$	+ 0.79
16.	$\text{Fe}^{3+} + \text{e}^- \longrightarrow \text{Fe}^{2+}$	+ 0.77
17.	$\text{I}_2 + 2\text{e}^- \longrightarrow 2\text{I}^-$	+ 0.535



S.No.	Reduction half cell reaction	E° in volts at 25°C
18.	$\text{Cu}^+ + \text{e}^- \longrightarrow \text{Cu}$	+ 0.53
19.	$\text{Cu}^{2+} + 2\text{e}^- \longrightarrow \text{Cu}$	+ 0.34
20.	$\text{Hg}_2\text{Cl}_2 + 2\text{e}^- \longrightarrow 2\text{Hg} + 2\text{Cl}^-$	+ 0.27
21.	$\text{AgCl} + \text{e}^- \longrightarrow \text{Ag} + \text{Cl}^-$	+ 0.222
22.	$\text{Cu}^{2+} + \text{e}^- \longrightarrow \text{Cu}^+$	+ 0.15
23.	$\text{Sn}^{4+} + 2\text{e}^- \longrightarrow \text{Sn}^{2+}$	+ 0.13
24.	$2\text{H}^+ + 2\text{e}^- \longrightarrow \text{H}_2$	0.00
25.	$\text{Fe}^{3+} + 3\text{e}^- \longrightarrow \text{Fe}$	- 0.036
26.	$\text{Pb}^{2+} + 2\text{e}^- \longrightarrow \text{Pb}$	- 0.126
27.	$\text{Sn}^{2+} + 2\text{e}^- \longrightarrow \text{Sn}$	- 0.14
28.	$\text{AgI} + \text{e}^- \longrightarrow \text{Ag} + \text{I}^-$	- 0.151
29.	$\text{Ni}^{2+} + 2\text{e}^- \longrightarrow \text{Ni}$	- 0.25
30.	$\text{Co}^{2+} + 2\text{e}^- \longrightarrow \text{Co}$	- 0.28
31.	$\text{Cd}^{2+} + 2\text{e}^- \longrightarrow \text{Cd}$	- 0.403
32.	$\text{Cr}^{3+} + \text{e}^- \longrightarrow \text{Cr}^{2+}$	- 0.41
33.	$\text{Fe}^{2+} + 2\text{e}^- \longrightarrow \text{Fe}$	- 0.44
34.	$\text{Cr}^{3+} + 3\text{e}^- \longrightarrow \text{Cr}$	- 0.74
35.	$\text{Zn}^{2+} + 2\text{e}^- \longrightarrow \text{Zn}$	- 0.762
36.	$2\text{H}_2\text{O} + 2\text{e}^- \longrightarrow \text{H}_2 + 2\text{OH}^-$	- 0.828
37.	$\text{Mn}^{2+} + 2\text{e}^- \longrightarrow \text{Mn}$	- 1.18
38.	$\text{Al}^{3+} + 3\text{e}^- \longrightarrow \text{Al}$	- 1.66
39.	$\text{H}_2 + 2\text{e}^- \longrightarrow 2\text{H}^-$	- 2.25
40.	$\text{Mg}^{2+} + 2\text{e}^- \longrightarrow \text{Mg}$	- 2.37
41.	$\text{Na}^+ + \text{e}^- \longrightarrow \text{Na}$	- 2.71
42.	$\text{Ca}^{2+} + \text{e}^- \longrightarrow \text{Ca}$	- 2.87
43.	$\text{Ba}^{2+} + 2\text{e}^- \longrightarrow \text{Ba}$	- 2.90
44.	$\text{Cs}^+ + \text{e}^- \longrightarrow \text{Cs}$	- 2.92
45.	$\text{K}^+ + \text{e}^- \longrightarrow \text{K}$	- 2.93
46.	$\text{Li}^+ + \text{e}^- \longrightarrow \text{Li}$	- 3.03

## SOLVED EXAMPLES

### OBJECTIVE

**Q.1** On passing  $C$  amperes of current through an electrolyte solution for  $t$  seconds,  $m$  gram of metal deposits on the cathode. The equivalent weight of the metal is

- (A)  $\frac{Ct}{m} \times 96500$       (B)  $\frac{Cm}{t} \times 96500$       (C)  $\frac{96500 \times m}{C \times t}$       (D)  $C \times t \times 96500 / m$

**Ans.** (C)

**Sol.** 1 Faraday, that is, 96500 coulombs deposits 1 gm equivalent of the substance. Now  $C \times t$  amount of electricity deposits ' $m$ ' gm of substance

$$\therefore 96500 \text{ C amount of electricity deposits} = \frac{96500 \times m}{C.t} = \text{equivalent weight}$$

**Q.2** One coulomb is equal to

- (A) 96500 Faraday      (B) charge on  $6.24 \times 10^{18}$  electrons  
(C) charge on 1 electron      (D) none of the above

**Ans.** (B)

**Sol.** Charge on  $6.023 \times 10^{23}$  electrons = 96500 C

$$\text{So, 1 coulomb would be the charge on } \frac{6.023 \times 10^{23}}{96500} = 6.24 \times 10^{18} \text{ electrons.}$$

**Q.3** If three Faradays (F) of electricity is passed through the solutions of  $\text{AgNO}_3$ ,  $\text{CuSO}_4$  and  $\text{AuCl}_3$ , the molar ratio of the cations deposited at the cathode is

- (A) 1 : 1 : 1      (B) 1 : 2 : 3      (C) 3 : 2 : 1      (D) 6 : 3 : 2

**Ans.** (D)

**Sol.** Since  $\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$ ,  $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$ ,  $\text{Au}^{3+} + 3\text{e}^- \rightarrow \text{Au}$ , three Faradays of electricity will deposit 3 moles of Ag, 1.5 moles of copper, and 1 mole of gold. Therefore, the molar ratio is 3 : 1.5 : 1 or 6 : 3 : 2.

**Q.4** During electrolysis of a concentrated aqueous solution of  $\text{NaCl}$ , the product at the cathode is

- (A) Na      (B)  $\text{Cl}_2$       (C)  $\text{O}_2$       (D)  $\text{H}_2$

**Ans** (B)

**Sol.** Chlorine gas is produced as chloride ions need a less voltage for oxidation to chlorine than needed by  $\text{H}_2\text{O}$  for oxidation to  $\text{O}_2$  (This extra voltage needed by water is called over voltage).

**Q.5** Two Pt electrodes fitted in a conductance cell are 1.5 cm apart and the cross-sectional area of each electrode is  $0.75 \text{ cm}^2$ . The cell constant is

- (A) 1.25      (B) 0.5 cm      (C)  $2.0 \text{ cm}^{-1}$       (D)  $0.2 \text{ cm}^{-1}$

**Ans.** (C)

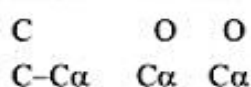
$$\text{Sol. Cell constant} = \frac{\ell}{a} = \frac{1.5}{0.75} = 2.0 \text{ cm}^{-1}$$

- Q.6** The ionisation constant of a weak electrolyte is  $25 \times 10^{-6}$  and the equivalent conductance of its 0.01 M solution is  $19.6 \text{ S cm}^2 \text{ eq}^{-1}$ . The equivalent conductance at infinite dilution of the electrolyte in  $\text{S cm}^2 \text{ eq}^{-1}$  is

(A) 250 (B) 196 (C) 392 (D) 384

**Ans.** (C)

**Sol.**  $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$



Or  $K = C\alpha^2$  Or  $25 \times 10^{-6} = 10^{-2} \cdot \alpha^2$

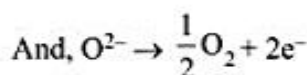
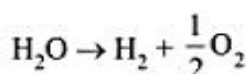
Or  $\alpha = 5 \times 10^{-2}$  Also  $\alpha = \frac{\lambda_v}{\lambda_\infty} = \frac{19.6}{\lambda_\infty}$  or  $\lambda_\infty = \frac{19.6}{5 \times 10^{-2}} = 392 \text{ S cm}^2 \text{ eq}^{-1}$

- Q.7** How many c.c. of oxygen is released by a current of 2 A flowing for 3 minutes and 13 seconds in acidulated water?

(A) 11.2 c.c. (B) 33.6 c.c. (C) 44.8 c.c. (D) 22.4 c.c.

**Ans.** (D)

**Sol.**  $Q = 2 \times 193 = 386 \text{ C}$



2 mole of electrons =  $2 \times 96500 \text{ C}$  give  $1/2$  mole of oxygen i.e.,  $11,200 \text{ cm}^3$ .

So, 386 C will give  $\frac{386 \times 11,200}{2 \times 96,500} = 22.4 \text{ c.c. of oxygen.}$

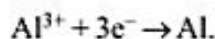
- Q.8** The cost of electricity required to deposit 1 g of Mg is Rs. 5.00. How much would it cost to deposit 10.0 g of Al? (Al = 27, Mg = 24)

(A) Rs.10.0 (B) Rs. 27.0 (C) Rs. 44.44 (D) Rs. 66.67

**Ans.** (D)

**Sol.**  $\text{Mg}^{2+} + 2\text{e}^- \rightarrow \text{Mg}$

$$\text{Quantity of electricity required to deposit 1.0 g of Mg} = \frac{2 \times 96500}{24}$$



$$\text{Quantity of electricity required to deposit 10.0 g of Al} = \frac{3 \times 96500}{27} \times 10$$

$$\text{Cost} = \frac{3 \times 96500}{27} \times \frac{10 \times 5 \times 24}{2 \times 96500} = \text{Rs. 66.67}$$

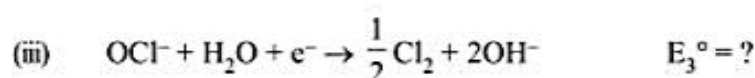
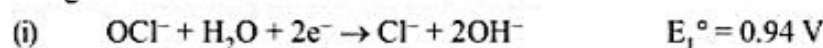
**Q.9** The standard electrode potential ( $E^\circ$ ) for  $\text{OCl}^-/\text{Cl}^-$  and  $\text{Cl}^-/\frac{1}{2}\text{Cl}_2$  respectively are 0.94 V and -1.36 V.

The  $E^\circ$  value for  $\text{OCl}^-/\frac{1}{2}\text{Cl}_2$  will be

- (A) -0.42 V (B) -2.20 V (C) 0.52 V (D) 1.04 V

**Ans.** (C)

**Sol.** The given half cell reactions can be written as



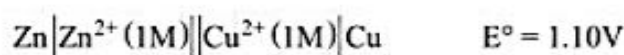
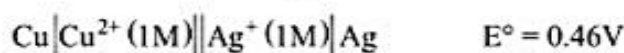
Now consider free energies ( $\Delta G^\circ = -nE^\circ F$ )

$$\Delta G_3^\circ = \Delta G_1^\circ + \Delta G_2^\circ$$

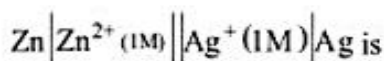
$$-1 \times F \times E_3^\circ = -2 \times F(0.94) - 1 \times F(-1.36)$$

$$E_3^\circ = 2 \times 0.94 - 1.36 = 0.52 \text{ V}$$

**Q.10** The e.m.f of the following cells is given

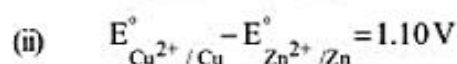
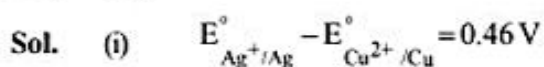


The e.m.f of the cell



- (A) 1.56 V (B) 0.64 V (C) -1.56 V (D) 2.02 V

**Ans.** (A)



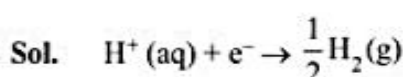
On adding (i) and (ii)

$$E_{\text{Ag}^+/\text{Ag}}^\circ - E_{\text{Zn}^{2+}/\text{Zn}}^\circ = 1.56 \text{ V}$$

**Q.11** A hydrogen electrode is dipped in a solution of pH = 3.0 at 25°C. The potential of the cell will be

- (A) 0.177 V (B) 0.087 V (C) -0.177 V (D) 0.059 V

**Ans.** (C)





$$E = E^\circ - \frac{0.059}{n} \log \frac{1}{(H^+)} = 0 - \frac{0.059}{1} \cdot \text{pH}$$

Or  $E = -0.059 \times 3 = -0.177$

**Q.12** In the cell



$E_{\text{cell}} - E^\circ_{\text{cell}} = 0.0591$  V. The ratio of  $C_1/C_2$  at 298 K is

- (A) 2.0 (B) 100 (C)  $10^{-2}$  (D) 1.0

**Ans.** (C)

**Sol.**  $\text{Zn} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu}$

$$E_{\text{cell}} - E^\circ_{\text{cell}} = -\frac{0.0591}{2} \log \frac{C_1}{C_2}$$

Or  $0.0591 = -\frac{0.0591}{2} \log \frac{C_1}{C_2}$  Or  $\log \left( \frac{C_1}{C_2} \right) = -2$  or  $\frac{C_1}{C_2} = \text{antilog } -2 = 10^{-2}$

**Q.13** The solution of nickel sulphate, in which a nickel rod is dipped, has been diluted 10 times. The potential of the nickel electrode

- (A) decreases by 60 mV (B) increases by 30 mV (C) decreases by 30 mV (D) increases by 60 mV

**Ans.** (C)

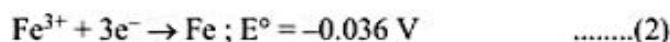
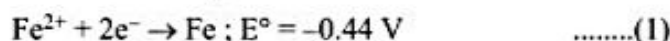
**Sol.**  $\text{Ni}^{2+} + 2e^- \rightarrow \text{Ni (s)}$

$$E = E^\circ - \frac{0.059}{2} \log \frac{1}{x}$$

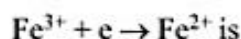
After dilution  $E = E^\circ - \frac{0.059}{2} \log \frac{10}{x}$

Therefore, the potential decreases by  $\frac{0.059}{2} \log 10 = 0.0295$  V or 0.03 V or 30.0 mV.

**Q.14** Given standard electrode potentials



The standard electrode potential  $E^\circ$  for



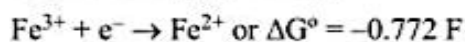
- (A) -0.476 V (B) -0.404 V (C) 0.404 V (D) +0.772 V

**Ans.** (D)

**Sol.**  $\text{Fe}^{2+} + 2e^- \rightarrow \text{Fe} \Delta G_1^\circ = -nE^\circ F = -2F(-0.44) = 0.88 F \quad \text{.....(1)}$

$\text{Fe}^{3+} + 3e^- \rightarrow \text{Fe} \Delta G_2^\circ = -nE^\circ F = -3F(-0.036) = 0.108 F \quad \text{.....(2)}$

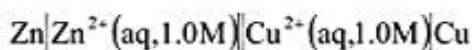
On subtracting (1) from (2)



$$\text{Or } \Delta G^\circ = -nE^\circ F = -0.772 F \quad \text{Or } E^\circ = \frac{0.772}{1} = 0.772 \text{ V}$$

## SUBJECTIVE

**Q.15** Consider the cell



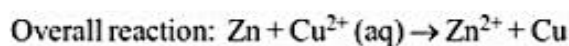
The standard reduction potentials are 0.350 V for  $\text{Cu}^{2+} (\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}$  and -0.763 V for  $\text{Zn}^{2+} (\text{aq}) + 2\text{e}^- \rightarrow \text{Zn}$

(a) What is the cell reaction?

(b) Calculate the e.m.f of the cell.

(c) Is the cell reaction spontaneous?

**Sol.** Anodic reaction:  $\text{Zn} \rightarrow \text{Zn}^{2+} (\text{aq}) + 2\text{e}^-$



$$\text{e.m.f of the cell } E_{\text{Cell}}^\circ = E_{\text{R}}^\circ - E_{\text{L}}^\circ = 0.350 - (-0.763) = 1.113 \text{ V}$$

Since  $E_{\text{Cell}}^\circ$  is positive, the  $\Delta G$  of the reaction ( $= -nEF$ ) will be negative and so the reaction is spontaneous.

**Q.16** Calculate the electrode potential of a copper wire dipped in 0.1 M  $\text{CuSO}_4$  solution at  $25^\circ\text{C}$ . The standard electrode potential of copper is 0.34 V.

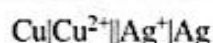
**Sol.** The electrode reaction is  $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$ .

$$\text{By using Nernst equation, } E = E^\circ - \frac{0.0591}{2} \log \frac{1}{[\text{Cu}^{2+}]}$$

$$\begin{aligned} \text{Or } E &= 0.34 - \frac{0.0591}{2} \log \frac{1}{0.1} = 0.34 - 0.02955 \\ &= 0.31045 \text{ V} \end{aligned}$$

**Q.17** The standard reduction potential of  $\text{Cu}^{2+}|\text{Cu}$  and  $\text{Ag}^+|\text{Ag}$  electrodes are 0.337 V and 0.799 V respectively. Construct a working cell with positive e.m.f. If the concentration of  $\text{Cu}^{2+}$  ions is 0.01 M, then for what concentration of  $\text{Ag}^+$  will the e.m.f of the cell be zero at  $25^\circ\text{C}$ ?

**Sol.** Since the reduction potential of silver electrode  $E^\circ_{\text{Ag}^+/\text{Ag}}$  is higher than copper electrode, the half cell  $\text{Ag}^+|\text{Ag}$  will constitute the cathode of the cell and the cell is



The cell reaction is  $\text{Cu} + 2\text{Ag}^+ \rightarrow \text{Cu}^{2+} + 2\text{Ag}$  and the standard e.m.f

$$E^\circ = 0.799 - 0.337 = 0.462 \text{ V.}$$

The Nernst equation for the cell is

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{2} \log \frac{[\text{Cu}^{2+}]}{[\text{Ag}^+]^2}$$

$$\text{Or } E_{\text{cell}} = 0 = 0.462 - \frac{0.0591}{2} \log \frac{[0.01]}{[\text{Ag}^+]^2}$$

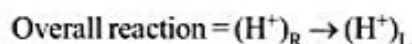
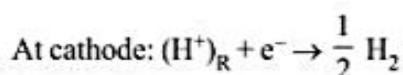
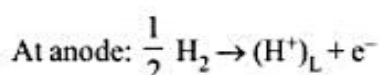
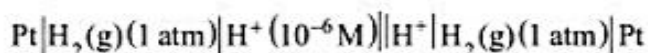
$$\text{Or } \log \frac{[0.01]}{[\text{Ag}^+]^2} = \frac{0.462 \times 2}{0.0591} = 15.6345$$

$$\text{Or } 2 \log [\text{Ag}^+] = \log [0.01] - 15.6345 = \frac{-2 - 15.6345}{2} = -8.8173$$

$$\text{Or } [\text{Ag}^+] = 1.523 \times 10^{-9} \text{ M}$$

**Q.18** A cell contains two hydrogen electrodes. The negative electrode is in contact with a solution of  $10^{-6} \text{ M}$  hydrogen ions. The e.m.f of the cell is 0.118 V at  $25^\circ\text{C}$ . Calculate the concentration of hydrogen ions at the positive electrode.

**Sol.** The cell is



$$\text{The cell potential is } E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{nF} \log \frac{(\text{H}^+)_\text{L}}{(\text{H}^+)_\text{R}}$$

$$\text{Or } 0.118 \text{ V} = 0 - \frac{0.059}{1} \log \frac{10^{-6}}{[\text{H}^+]} \quad \text{Or } [\text{H}^+] = 10^{-4} \text{ M}$$

**Q.19** Zinc granules are added in excess to 500 mL of 1.0 M nickel nitrate solution at 25°C until equilibrium is reached. If the standard reduction potential of  $\text{Zn}^{2+}/\text{Zn}$  and  $\text{Ni}^{2+}/\text{Ni}$  are  $-0.75\text{ V}$  and  $-0.24\text{ V}$  respectively, calculate the concentration of  $\text{Ni}^{2+}$  in the solution at equilibrium.

**Sol.** The cell reaction is  $\text{Zn} + \text{Ni}^{2+} \rightarrow \text{Zn}^{2+} + \text{Ni}$ .

$E^\circ$ , the standard e.m.f, is  $-0.24 - (-0.75) = 0.51\text{ V}$ .

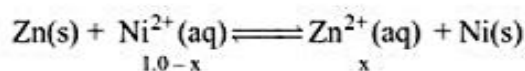
The equilibrium constant of the reaction  $K$  is  $[\Delta G^\circ = -nE^\circ F = -RT \ln K]$ ,

given by the expression

$$\log K = \frac{nE^\circ F}{2.303 RT} = \frac{(2 \times 96500 \text{ C mol}^{-1})(0.51)}{(2.303)(8.314 \text{ JK}^{-1})(298)}$$

$$\text{Or } K = 1.78 \times 10^{-17}$$

Let 'x' be the concentration of  $\text{Zn}^{2+}$  ions. Then



$$K = 1.78 \times 10^{-17} = \frac{[\text{Zn}^{2+}]}{[\text{Ni}^{2+}]} = \frac{x}{(1.0-x)} \text{ or } K(1.0-x) = x$$

$$\therefore x = \frac{K(1.0)}{1+K} \simeq 1.0 \text{ M}$$

$$[\text{Ni}^{2+}] = \frac{[\text{Zn}^{2+}]}{K} = \frac{1.0 \text{ M}}{1.78 \times 10^{17}} = 5.6 \times 10^{-18} \text{ M}$$

**Q.20** How many coulombs of electricity are required for the following reactions?

(i) 1.0 mol of  $\text{Cu}^{2+}$  to Cu and

(ii) 1.0 mol of  $\text{KMnO}_4$  to  $\text{MnSO}_4$

**Sol.** (i) The reaction is  $\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$  and for this the quantity of electricity required is 2 Faradays, as two mole of electrons are involved. Therefore,  $2 \times 96500 = 193000$  coulombs of electricity is required.

(ii) For the reaction  $\text{MnO}_4^-$  to  $\text{Mn}^{2+}$ , 5 moles of electrons are involved  $\text{Mn}^{7+} + 5e^- \rightarrow \text{Mn}^{2+}$  and for this the quantity of electricity required is  $5 \times 96500 = 482500$  coulombs.

**Q.21** How long a current of 3 A has to be passed through a solution of silver nitrate to coat a metal surface of  $80 \text{ cm}^2$  with a  $0.005 \text{ mm}$  thick layer. Density of silver is  $10.5 \text{ g cm}^{-3}$ .

**Sol.** Volume of metal to be deposited =  $(80 \text{ cm}^2)(0.0005 \text{ cm}) = 0.04 \text{ cm}^3$

Mass of metal to be deposited =  $(10.5)(0.04) = 0.42 \text{ gm}$

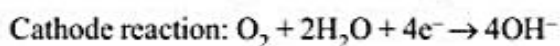
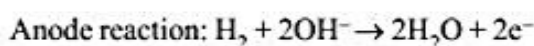
$$\text{Amount of silver to be deposited} = \frac{0.42}{108.0} = 3.889 \times 10^{-3} \text{ moles}$$

$$\text{Amount of electricity necessary} = \underset{(\text{moles})}{3.889 \times 10^{-3}} \times 96500 \text{ C mol}^{-1} = 375.27 \text{ C}$$

$$\text{Time for which 3 A current is to be passed} = \frac{375.27}{3} = 125.09 \text{ sec.}$$



- Q.22** In a fuel cell, hydrogen and oxygen react to produce electricity. In the process, hydrogen gets oxidised at the anode and oxygen gets reduced at the cathode. If 67.2 L of  $H_2$  at STP reacts in 15 minutes, what is the average current produced? If the entire current is used for electro-deposition of copper from copper (II) in solution, what mass of copper is deposited?



**Sol.** Amount of hydrogen oxidised =  $\frac{67.2}{22.4} = 3$  moles

Amount of electrons produced =  $2 \times 3$  moles of electrons

Electricity produced =  $2 \times 3 \times 96500$  C

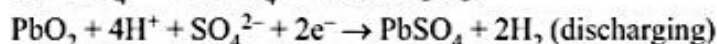
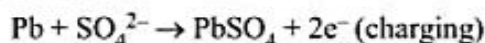
Current produced =  $2 \times 3 \times 96500 / 15 \times 60 = 643.33$  A

1.0 mole of copper gets deposited by the absorption of 2 moles of electrons

Amount of Cu deposited = 3 moles

Or, mass of Cu deposited =  $3 \times 63.5 = 190.5$  gm

- Q.23** During the discharge of a lead storage battery, the density of sulphuric acid fell from  $1.294 \text{ g mL}^{-1}$  to  $1.139 \text{ g mL}^{-1}$ . Sulphuric acid of density  $1.294 \text{ g mL}^{-1}$  is 39%  $H_2SO_4$  by mass and that of density  $1.139 \text{ g mL}^{-1}$  is 20%  $H_2SO_4$  by mass. The battery holds 3.5 L of acid and the volume remains practically constant during the discharge. Calculate the number of ampere hour for which the battery has been used. The reactions are



**Sol.** Mass of  $H_2SO_4$  (initially) =  $3.5 \times 10^3 \times 1.294 = 4529$  gm

$$\text{Actual mass of } H_2SO_4 = \frac{39}{100} \times 4529 = 1766.3 \text{ gm}$$

$$\text{Mass of } H_2SO_4 \text{ in the end} = 1.139 \times 3.5 \times 10^3 = 3986.5 \text{ gm}$$

$$\text{Actual mass of } H_2SO_4 = \frac{20}{100} \times 3986.5 = 797.3 \text{ gm}$$

$$\text{Mass of } H_2SO_4 \text{ consumed} = 1766.3 - 797.3 = 969.0 \text{ gm}$$

$$\text{Moles of } H_2SO_4 \text{ consumed} = \frac{969}{98} = 9.888 \text{ moles}$$

Amount of  $H^+$  consumed =  $2 \times 9.888$  moles (since  $H_2SO_4$  has  $2H^+$ ). In the discharge reaction, 4 moles of  $H^+$  are consumed per 2 moles of electrons. Therefore, electrons discharged  $(2 \times 9.888) \times 2/4 = 9.888$  moles of electrons. So, the amount of electricity discharged =  $9.888 \text{ moles} \times 96,500 \text{ C} = 954192 \text{ C}$ .

Battery has been used for =  $954192/60 \times 60 = 265.05$  ampere hours.

- Q.24** 19.0 grams of molten  $SnCl_2$  is electrolysed for some time by using inert electrodes, until 0.119 g of Sn is deposited at the cathode. No substance is lost during electrolysis. Find the ratio of masses of  $SnCl_2$  and  $SnCl_4$  after electrolysis.

**Sol.** Cathode:  $\text{Sn}^{2+} + 2\text{e}^- \rightarrow \text{Sn}$ ; Anode:  $\text{Sn}^{2+} \rightarrow \text{Sn}^{4+} + 2\text{e}^-$

Since 0.119 g of Sn is deposited at cathode then 0.119 g of  $\text{Sn}^{4+}$  must have formed at anode (see the electrode reactions). So, a total of  $2 \times 0.119$  g of  $\text{Sn}^{2+}$  are lost from the solution.

$$\begin{aligned}\text{Mass of remaining SnCl}_2 &= 19 \text{ g} - \frac{M_{\text{SnCl}_2}}{M_{\text{Sn}}} \times m_{\text{Sn}} \\ &= 19 - \frac{189.6}{119} \times 2 \times 0.119 = (19 - 0.379) = 18.621 \text{ g}\end{aligned}$$

$$\text{Mass of SnCl}_4 \text{ formed} = \frac{M_{\text{SnCl}_4}}{M_{\text{Sn}}} \times m_{\text{Sn}} = \frac{260.2}{119} \times 0.119 = 0.26 \text{ g}$$

$$\frac{m(\text{SnCl}_2)}{m(\text{SnCl}_4)} = \frac{18.621}{0.260} = \frac{71.62}{1}$$

**Q.25** How many grams of silver could be plated out on a serving tray by electrolysis of a solution containing silver in +1 oxidation state for a period of 8 hours at a current of 8.46 amperes. What is the area of the tray if the thickness of the silver plating is 0.00254 cm? The density of silver is 10.5 g/cm<sup>3</sup>.

**Sol.**  $m = \frac{It}{F} \cdot \frac{M}{z} = \frac{(8.46)(8 \times 60 \times 60)(107.8)}{(96500 \text{ C mol}^{-1})} = 272.18 \text{ g}$

$$\text{Volume of silver plated out } V = \frac{m}{\rho} = \frac{272.18}{10.5} = 25.92 \text{ cm}^3$$

$$\text{Area of tray plated} = \frac{25.92}{0.00254} = 10204.7 \text{ cm}^2$$

**Q.26** One of the methods of preparation of per disulphuric acid,  $\text{H}_2\text{S}_2\text{O}_8$ , involve electrolytic oxidation of  $\text{H}_2\text{SO}_4$  at anode ( $2\text{H}_2\text{SO}_4 \rightarrow \text{H}_2\text{S}_2\text{O}_8 + 2\text{H}^+ + 2\text{e}^-$ ) with oxygen and hydrogen as by-products. In such an electrolysis, 9.722 L of  $\text{H}_2$  and 2.35 L of  $\text{O}_2$  were generated at STP. What is the weight of  $\text{H}_2\text{S}_2\text{O}_8$  formed?

**Ans.** 43.49g

**Sol.** Equivalent in oxidation process = Equivalent in reduction process

Equivalent of  $[\text{H}_2\text{S}_2\text{O}_8 + \text{O}_2] = \text{Equivalent of } \text{H}_2$

$$n_{\text{H}_2\text{S}_2\text{O}_8} \times 2 + \frac{2.35}{22.4} \times 4 = \frac{9.722}{22.4} \times 2$$

$$n_{\text{H}_2\text{S}_2\text{O}_8} \times 2 + 0.4196 = 0.868$$

$$n_{\text{H}_2\text{S}_2\text{O}_8} = 0.2242 \text{ m}$$

$$\text{wt. of } \text{H}_2\text{S}_2\text{O}_8 = 0.2242 \times 194 = 43.49 \text{ gm}$$

**Q.27** A dilute aqueous solution of KCl was placed between two electrodes 10 cm apart, across which a potential of 6 volt was applied. How far would the  $K^+$  ion move in 2 hours at  $25^\circ\text{C}$ ? Ionic conductance of  $K^+$  ion at infinite dilution at  $25^\circ\text{C}$  is  $73.52 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$

**Ans.** 3.29 cm

**Sol.**  $\lambda = \mu F$

$$\mu = \frac{\text{velocity}}{\text{Potential gradient}} = \frac{\lambda}{F}$$

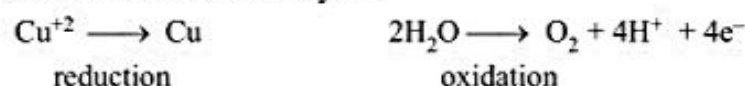
$$\frac{\text{distance} / 2 \times 3600}{6/10} = \frac{73.52}{96500}$$

$$\text{distance} = \frac{73.52}{96500} \times \frac{6}{10} \times 2 \times 3600 = 3.29 \text{ cm}$$

**Q.28** An acidic solution of  $\text{Cu}^{2+}$  salt containing 0.4 g of  $\text{Cu}^{2+}$  is electrolyzed until all the copper is deposited. The electrolysis is continued for seven more minutes with the volume of solution kept at 100 ml and the current at 1.2 amp. Calculate the volume of gases evolved at NTP during the entire electrolysis.

**Ans.**  $V(\text{O}_2) = 99.68 \text{ mL}$ ,  $V(\text{H}_2) = 58.49 \text{ mL}$ , Total vol. = 158.17 mL

**Sol.** solution of Cu salt electrolysed



Initially Equivalent of  $\text{Cu}^{+2} = \text{Equivalent of O}_2$

$$\frac{0.4}{63.5} \times 2 = n_{\text{O}_2} \times 4$$

$$n_{\text{O}_2} \text{ released at anode} = 3.14 \times 10^{-3}$$

charge transfer in next seven minutes

$$q = It = \frac{1.2 \times 7 \times 60}{96500} = 5.22 \times 10^{-3}$$

eq. of  $\text{H}_2$  released

$$\text{due to further reduction} = 5.22 \times 10^{-3} \Rightarrow n_{\text{H}_2} = 2.61 \times 10^{-3}$$

eq. of  $\text{O}_2$  released

$$\text{due to further oxidation} = 5.22 \times 10^{-3} \Rightarrow n_{\text{O}_2} = 1.3 \times 10^{-3}$$

$$\begin{aligned} \text{Total volume of H}_2 \text{ released} &= 2.61 \times 10^{-3} \times 22.4 \times 100 \text{ ml} \\ &= 58.49 \text{ ml} \end{aligned}$$

$$\begin{aligned} \text{Total volume of O}_2 \text{ released} &= (3.14 \times 10^{-3} + 1.3 \times 10^{-3}) \times 22400 \text{ ml} \\ &= 99.68 \text{ ml} \end{aligned}$$

$$\text{Total volume } 58.49 + 99.68 = 158.17 \text{ ml}$$

**Q.29** Estimate the cell potential of a Daniel cell having 1 M  $\text{Zn}^{2+}$  & originally having 1 M  $\text{Cu}^{2+}$  after sufficient  $\text{NH}_3$  has been added to the cathode compartment to make  $\text{NH}_3$  concentration 2 M.

$K_f$  for  $[\text{Cu}(\text{NH}_3)_4]^{2+} = 1 \times 10^{12}$ ,  $E^0$  for the reaction,

$\text{Zn} + \text{Cu}^{2+} \longrightarrow \text{Zn}^{2+} + \text{Cu}$  is 1.1 V.

**Ans.**  $E^0 = 0.610\text{V}$

**Sol.**

Anode	Cathode
$\text{Zn} \text{Zn}^{2+}$	$\text{Cu} \text{Cu}^{2+}$
$\text{Cu}^{2+} + 4\text{NH}_3 \longrightarrow [\text{Cu}(\text{NH}_3)_4]^{2+}$	

Initially 1 M

finally x              2M              1M

$$1 \times 10^{12} = \frac{1}{x(2)^4}$$

$$x = 6.25 \times 10^{-14}$$

for reaction  $\text{Zn} + \text{Cu}^{2+} \longrightarrow \text{Zn}^{2+} + \text{Cu}$

$$E = E^0 - \frac{0.059}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

$$= 1.1 - \frac{0.059}{2} \log \frac{1}{6.25 \times 10^{-14}}$$

$$= 1.1 - (0.3895) = 0.610 \text{ V}$$



# NITROGEN COMPOUNDS

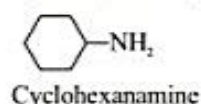
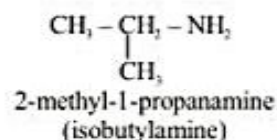
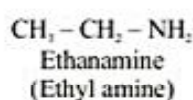
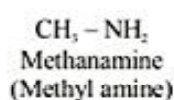
## AMINES

Amines are derivative of ammonia where one or more hydrogen atoms are replaced by alkyl or aryl groups.

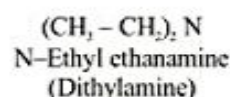
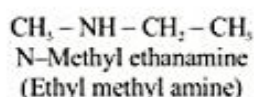
## CLASSIFICATION

Amines are classified as being primary ( $1^\circ$ ), secondary tertiary ( $3^\circ$ ) on the basis of the number of alkyl or aryl groups attached to the nitrogen.

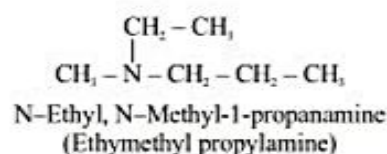
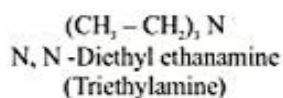
### (i) Primary amines :



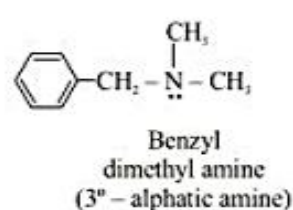
### (ii) Secondary Amine :



### (iii) Tertiary Amine :

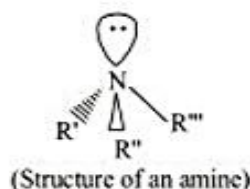


When all the alkyl or aryl groups are same the amine is called "simple", and "mixed" when these are different. Amines are divided into aliphatic amines and aromatic amines. In an aliphatic amines all the carbon bonded directly to nitrogen are derived from alkyl : In an aromatic amines one or more of the group bonded directly to nitrogen are aryl groups.



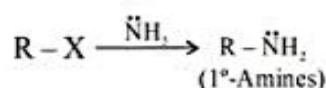
## STRUCTURES

The nitrogen atom of most amines is like that of ammonia; it is approximately  $sp^3$  hybridized. The three alkyl groups (or hydrogen atoms) occupy corner of a tetrahedron; the  $sp^3$  orbital containing the unshared electron pair is directed towards the other corner. We describe the shape of amines by the location of the atoms as being trigonal pyramidal.

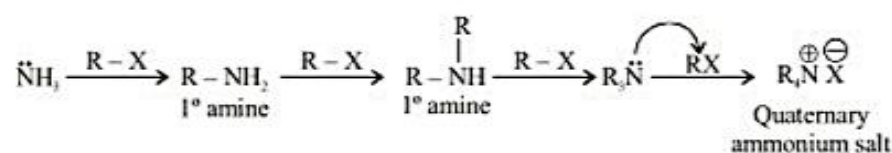


## METHODS OF PREPARATION

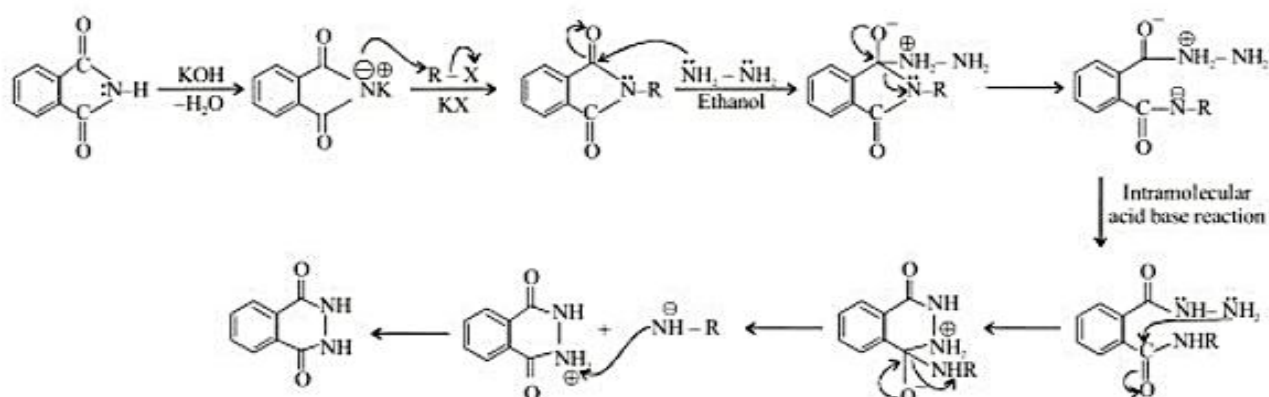
**By the ammonolysis of alkyl halide :** This method of preparation of amines involves nucleophilic substitution by ammonia or an amine molecule on an alkyl halide



To obtain the  $1^\circ$ -amine large amount of  $NH_3$  is used. If alkyl halide is taken in to excess then mixture of  $1^\circ, 2^\circ, 3^\circ$  amines of quaternary salt is obtained.

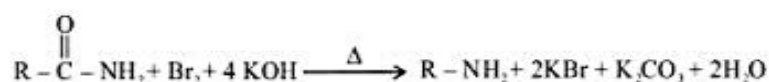
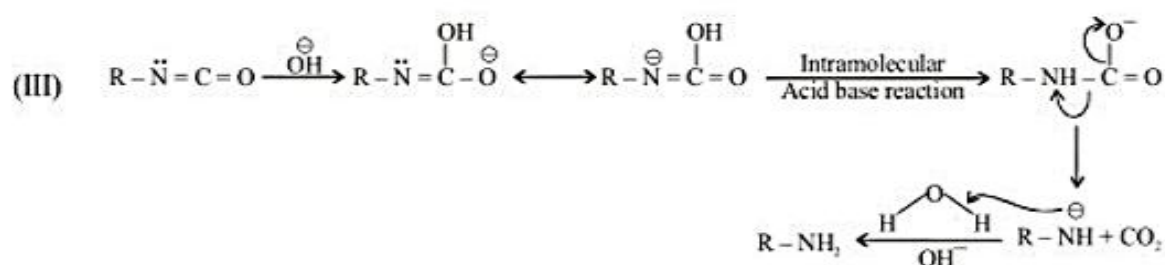
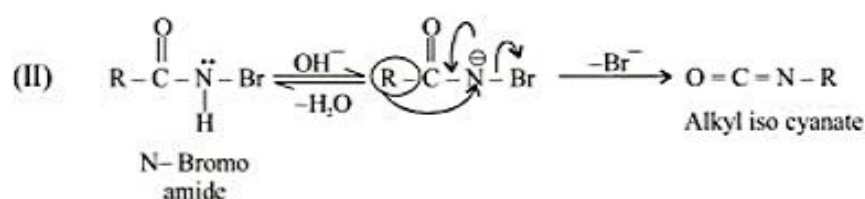
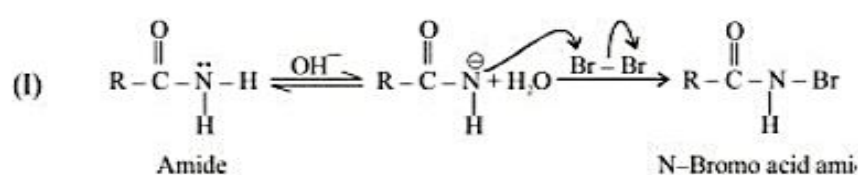


**Gabriel Phthalimide synthesis :** Potassium phthalimide can be used to prepare primary amines by the method known as Gabriel synthesis.

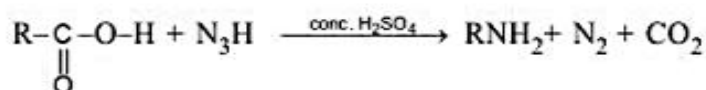


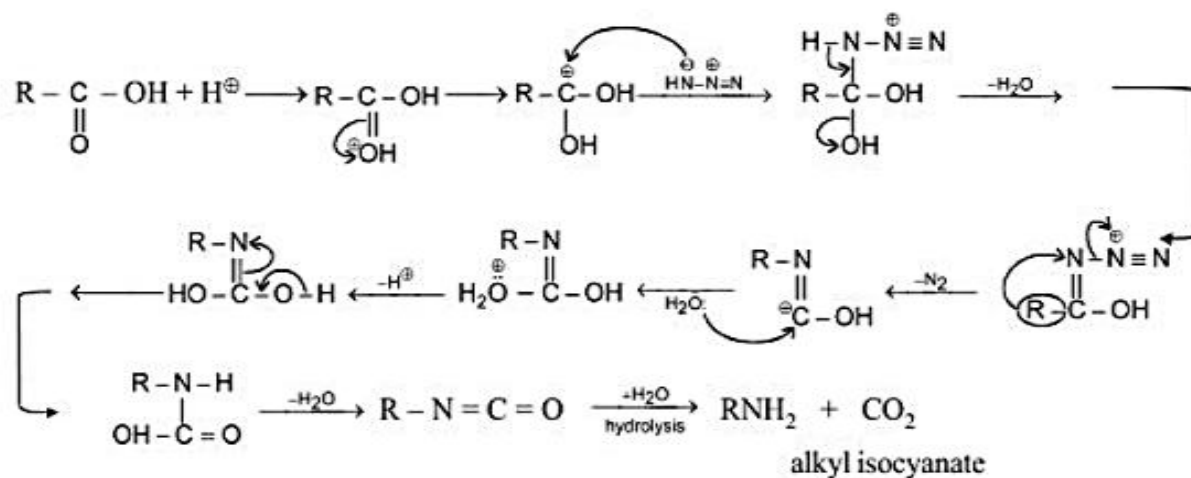
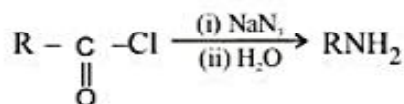
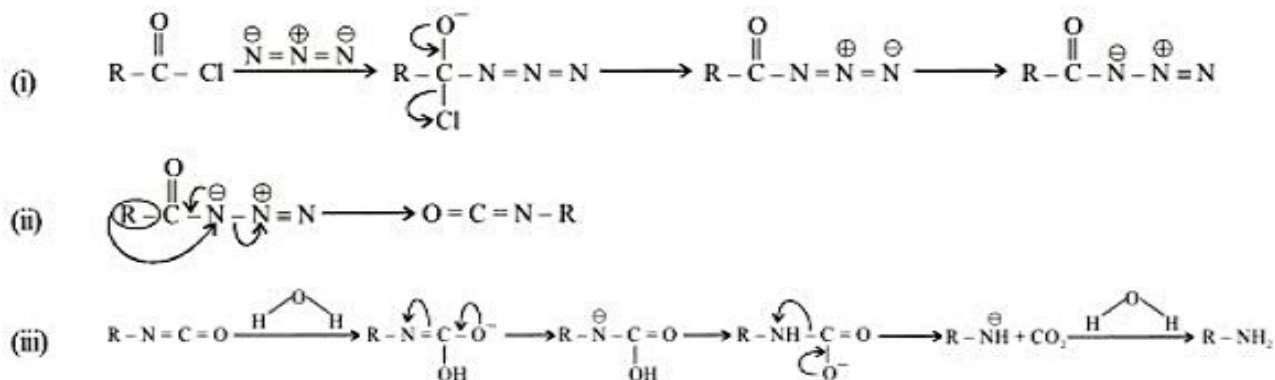
**By Hofmann Bromamide degradation reaction :**

Primary amide react with solution of bromine or chlorine in sodium hydroxide or potassium hydroxide to yield amines through a reaction known as Hofmann degradation or Hofmann rearrangement.

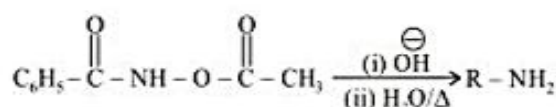
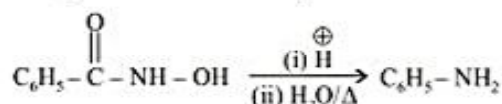
**Mechanism****Note :**

- (i) Intermediate products of this reaction is  $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}-\text{Br}$  &  $\text{R}-\text{N}=\text{C}=\text{O}$
- (ii) Migration of alkyl group is the r.d.s. (rate determine step) of the reaction. i.e. formation of  $\text{R}-\text{N}=\text{C}=\text{O}$  is r.d.s.
- (iii) No change takes place in the configuration of chiral carbon during migration of alkyl group.

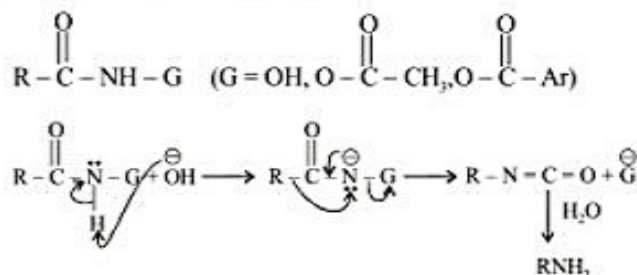
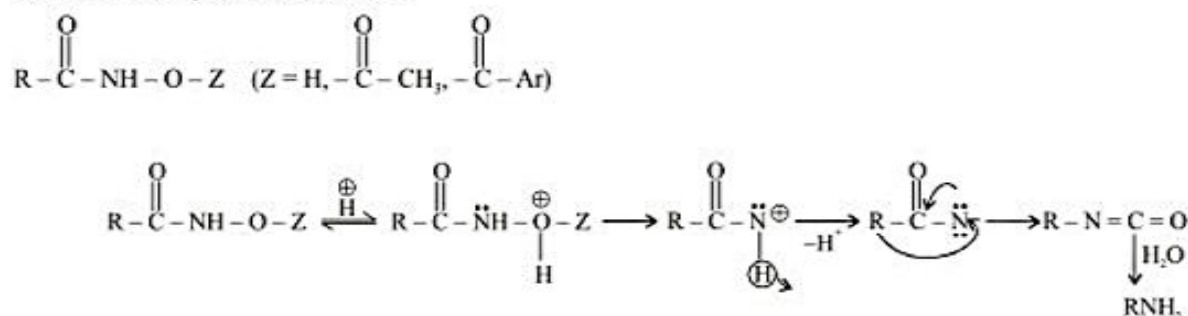
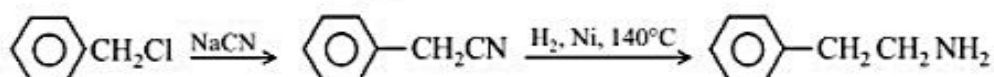
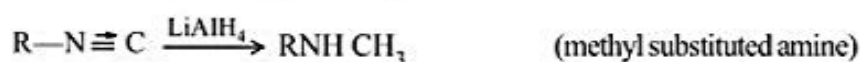
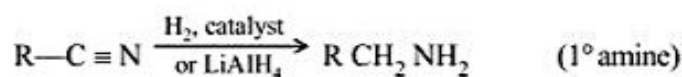
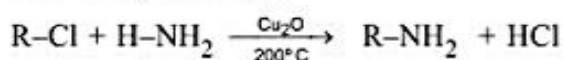
**From Alkanoic acid (Schmidt Reaction) :**

**Mechanism :-****Curtius Rearrangement :****Mechanisms****The Lossen Rearrangement**

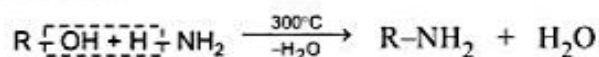
The thermal, acid or base catalysed, intramolecular conversion of hydroxamic acid and their O-acyl and O-aryl derivatives to isocyanate is called Lossen rearrangement.





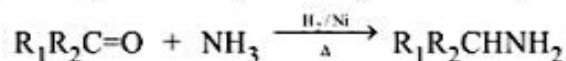
**Mechanism****(i) The base catalysed mechanism****(ii) The acid catalysed mechanism****By the Reduction of Nitriles and Iso-Nitriles****From Alkylchloride :**

**Note :** In the above reaction  $\text{Cu}_2\text{O}$  neutralises the evolved  $\text{HCl}$  in form of  $\text{Cu}_2\text{Cl}_2 + \text{H}_2\text{O}$  otherwise  $\text{HCl}$  forms additional salt with amines.

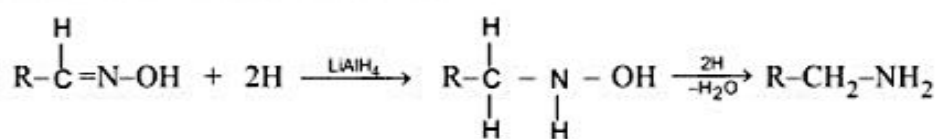
**From Grignard reagent :****From Alcohol :**

**By Aldehyde or Ketone (reaction with  $H_2$  and  $NH_3$  in presence of catalyst) :**

Primary amine can be produced by passing a mixture of aldehyde or ketone and large excess of ammonia and hydrogen under pressure (20-150 atm) over raney nickel catalyst at 40-150°C.



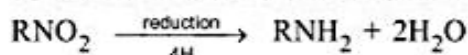
**Note :** Small amount of secondary and tertiary amines are also produced in this method as by products.

**From Alkyl isocyanate (Alkaline Hydrolysis) :****From Aldoxime (By Reduction) :**

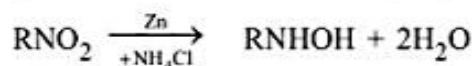
**By reduction of Nitro compounds :** Nitro alkanes are reduced catalytically to primary amine.

(a) By  $LiAlH_4$

(b) By Metal and acid (commonly used  $Sn + HCl$  or  $Fe + HCl$ )

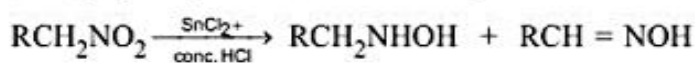


**Note : (i)** When reduction with metal is carried out in neutral solution e.g. with  $Zn$  dust &  $NH_4Cl$  solution, nitro compounds are converted into N-alkyl hydroxyl amine.



N-alkylhydroxyl amine

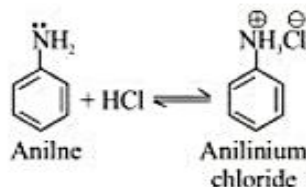
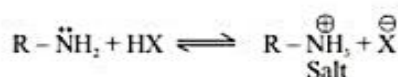
(ii) When reduction of nitroalkane is carried out with  $SnCl_2$  and conc.  $HCl$ , a mixture of N-alkyl hydroxyl amine and oxime are produced.



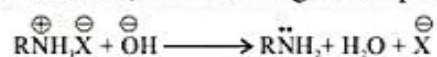
N-Alkyl hydroxy amine      Oxime

**BASIC CHARACTER OF AMINES**

Amines are relatively weak bases. They are stronger bases than water but are far weaker bases than hydroxides ions ( $OH^-$ ), alkoxide ions ( $RO^-$ ) and alkanide ( $R^-$ ) anions. These react with acids to form salts.

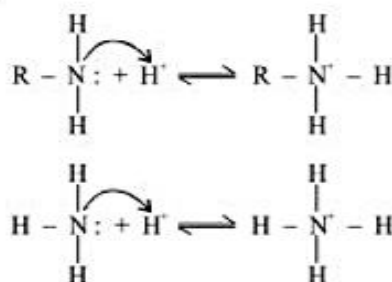


On reaction with a base such as NaOH, amine salt regenerate parent amine.



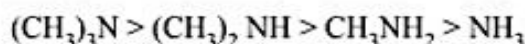
## BASICITY OF ALKANAMINES

Primary alkanamines ( $\text{RNH}_2$ ) are more basic than ammonia ( $\text{NH}_3$ ). Their reactions with proton can be used to compare their basicity.

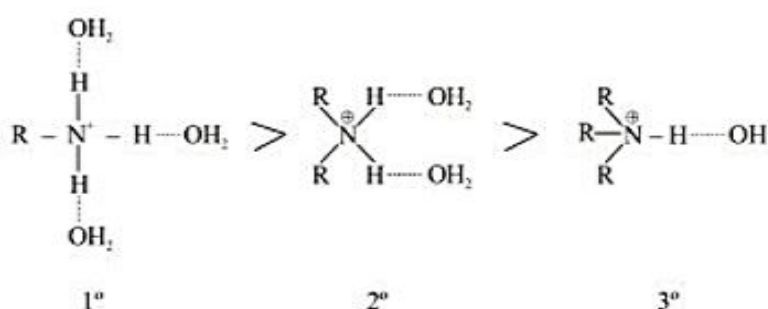


We can account for this on the basis of the electron-releasing ability of an alkyl group (R). An alkyl group releases electrons towards nitrogen, so the unshared electron pair becomes more available for sharing with proton of the acid. The substituted ammonium ion thus formed, gets stabilized as a result of positive charge dispersal by +I effect of the alkyl group. This makes alkylamines stronger bases than ammonia.

This explanation is supported by measurements showing that in the **gas phase**, the basicities of the following amines increase with increasing methyl substitution :



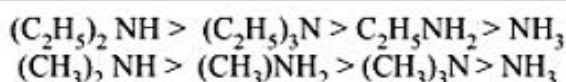
This is not the order of basicity of these amines in aqueous phase, however. In aqueous phase, the substituted ammonium cations get stabilized by +I effect of the alkyl group as well as solvation with water molecules. With a larger size of the ion, solvation and stability of the ion will be lesser. The stability order in aqueous phase is as follows :



When the stability of the substituted ammonium cation is greater, the corresponding amine as a base is stronger. The basicity order in aliphatic amines is  $1^\circ > 2^\circ > 3^\circ$ . This is the reverse of basicity order based on inductive effect.

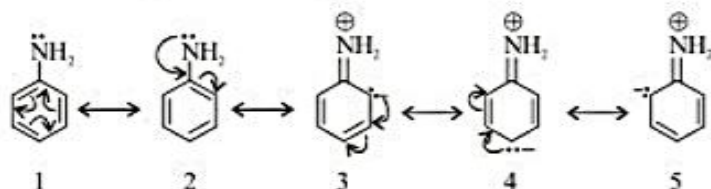
There is no steric hindrance to H bonding when the alkyl group is small. There is a difference in the basicity order in methyl and ethyl group and so on. Therefore, in aqueous state, inductive effect, solvation effect and steric hindrance of the alkyl group determine the basicity strength. The following examples show the basicity strength order in ethyl and methyl substituted amines.



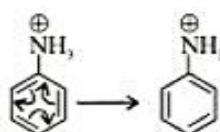
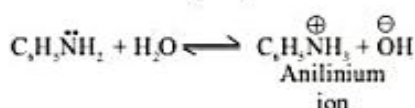


## BASICITY OF ARYLAMINES

The  $\text{pK}_\text{b}$  value of aniline is quite high because in aniline, the  $-\text{NH}_2$  group is directly attached to the benzene ring. The following contributors make aniline a resonance hybrid:



Structure 1 and 2 are the Kekule structures that contribute to any benzene derivative. Structures 3-5, however, delocalize the unshared electron pair of the nitrogen over the ortho and para position of the ring. This delocalization of the electron pair make it less available to a proton, and delocalization of the electron pair stabilizes aniline. When aniline accepts a proton it becomes an anilinium ion:

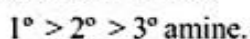


The higher the number of resonating structures, the greater is the stability. This makes aniline with five resonating structures more stable than the anilinium ion. Therefore, the basic nature of aniline or other arylamines is less than that of ammonia.

## PHYSICAL PROPERTIES

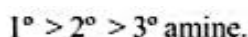
- (a) Like ammonia, amines are polar compounds and except  $3^\circ$  amines can form intermolecular H- bonds that's why they have higher boiling points.

Boiling points of  $1^\circ$ ,  $2^\circ$  and  $3^\circ$  amines follow the order.



- (b) Unlike other organic compounds, amines are much more soluble in water. Because All amines form a stronger H- bond with water.

- (c) Solubility in water follow the order.



It is all due to H- Bonding.

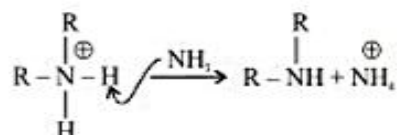
- (d) Boiling points of amines are lesser than alcohols and acids of comparable mol. weight. Because H-bonding in amines is less pronounced in  $1^\circ$  and  $2^\circ$  than that in alcohols and carboxylic acids. Because nitrogen is less electronegative than oxygen.

Thus every question regarding boiling point can be answered on the basis of H - bonding.

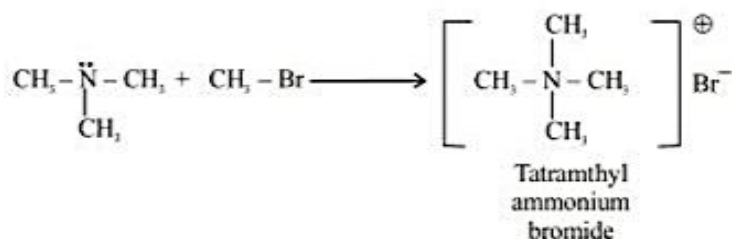
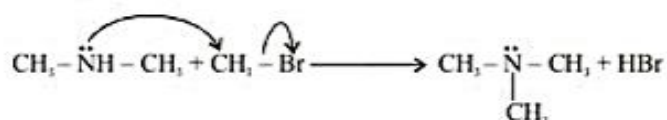
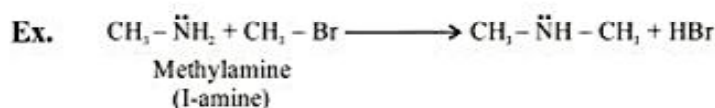


## CHEMICAL PROPERTIES

- (1) **Alkylation reaction :** Aliphatic amines undergo alkylation on treatment with an alkyl halide in a basic medium such as ammonia.



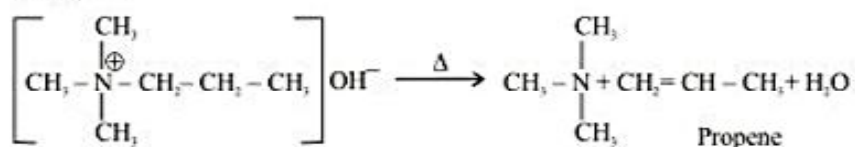
**Note :** - If alkyl halide is taken into excess then quaternary ammonium salt is obtained.



Quaternary ammonium halides are converted into their corresponding hydroxides on treatment with moist oxide or methanolic KOH.

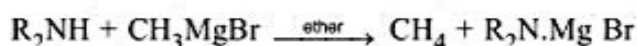
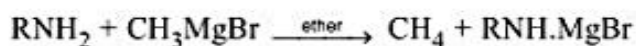


When a quaternary ammonium hydroxide is heated strongly, it decomposes to yield water, a tertiary amine and an alkene. For example Trimethyl-n-propylammonium hydroxide yields trimethylamine and propene.



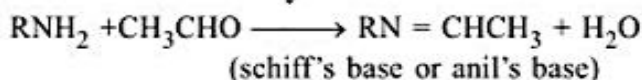
The reaction is called Hofmann elimination reaction.

**Reaction with Grignard reagent :** Since primary and secondary amines have active hydrogen, they on reaction with Grignard reagent give alkanes

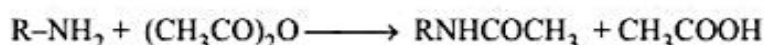


**Note :** Tertiary do not react because of absence of active hydrogen.

**Reaction with Aldehydes and Ketone:**



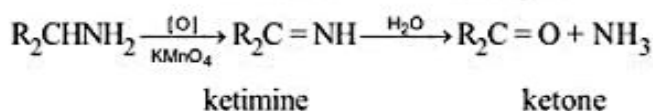
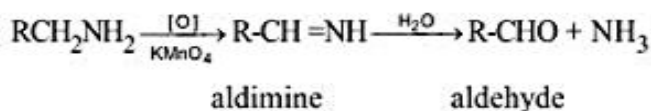
**Acylation :** 1° and 2° amines react with acetyl chloride or acetic anhydride to form acetyl derivatives.



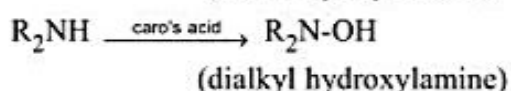
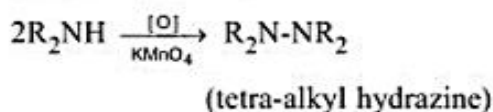
- Note :** (a) Tertiary amines do not undergo this reaction because of absence of replaceable H-atom.  
 (b) When Benzoyl chloride is used in place of acetyl chloride reaction is called '**Schotten - Baumann**' reaction.

**Oxidation :** All three are oxidised in different ways depending upon conditions of oxidation.

- (a) **Primary Amine :** Oxidised to aldehydes and ketones.

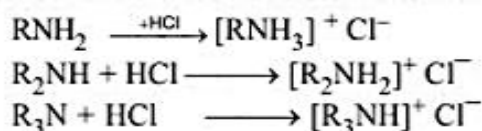


- (b) **Secondary Amine :**



- (c) **Tertiary Amine :** Resistant to  $\text{KMnO}_4$  but oxidised by neutral and aqueous  $\text{H}_2\text{O}_2$  in cold to form trialkyl amine oxide.

**Salt formation:** Amine forms salt with mineral acids



These salts may undergo dealkylation at higher temp.

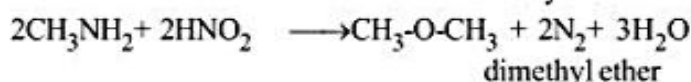
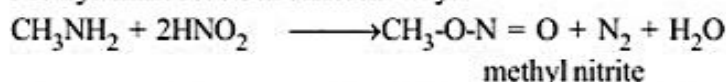
**For example :**  $\text{C}_2\text{H}_5\text{NH}_3^+\text{Cl}^- \xrightarrow{\Delta} \text{C}_2\text{H}_5\text{Cl} + \text{NH}_3$

**Reaction with  $\text{HNO}_2$  :** This reaction distinguishes 1°, 2° and 3° alcohols.

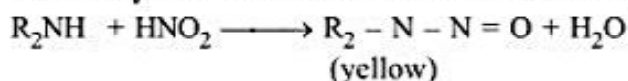
- (a) **Primary Amine :** Except methyl amine, reaction happens at ordinary temp. to evolve  $\text{N}_2$  Gas.



Methylamine reacts in different way:

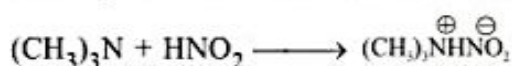


- (b) **Secondary Amine :** Form nitroso amines with  $\text{HNO}_2$  (No  $\text{N}_2$  gas is evolved)

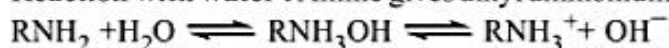


**Note :** These nitroso amines formed, on warming with phenol and conc.  $\text{H}_2\text{SO}_4$  give a brown or red colour changing to blue or green on further addition of an alkali, colour changes to red. This test is called **Libermann's nitroso test** and used for identification of 2° amines.

- (c) **Tertiary Amine :** These are inert to  $\text{HNO}_2$  but being basic in nature forms salts with it.



**Reaction with water :** Amine gives alkyl ammonium hydroxides which dissociate into ions-



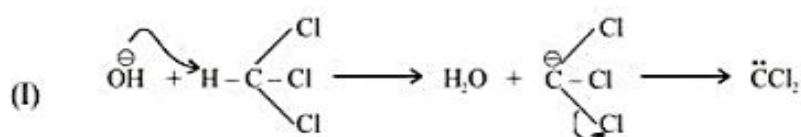
**Isocyanide test or Carbylamine reaction :**

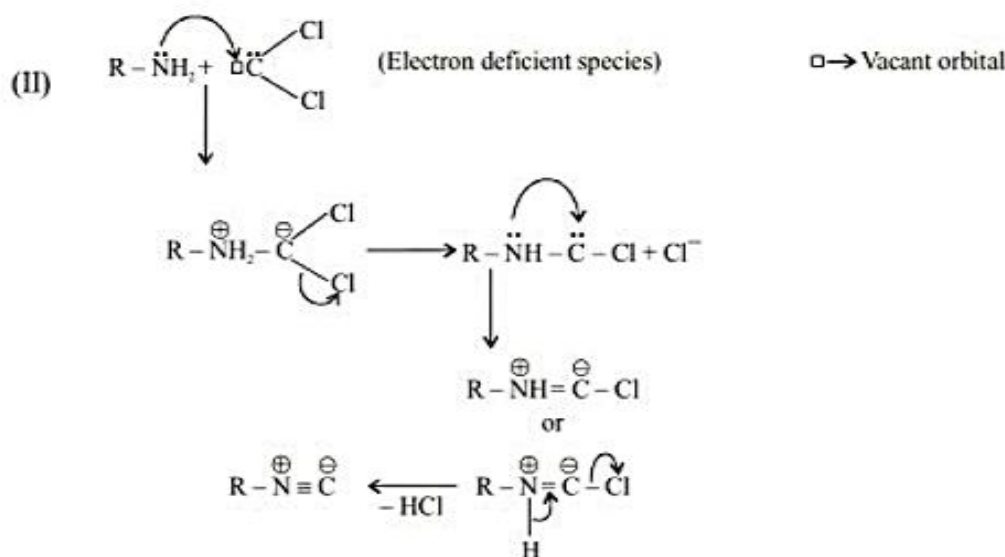
Primary amines when heated with chloroform and ethanolic KOH solution, alkyl isocyanides is produced which have characteristic foul smell. This reaction is characteristic to the primary amine. This test is known as **carbyl amine test or isocyanide test**.



**Mechanisms**

The reaction proceeds via the formation of dichloro carbene ( $:\text{CCl}_2$ ).



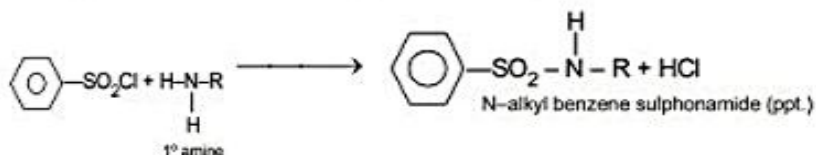


**Reaction with Hinsberg reagent :** This is a method for separation of 1°, 2° and 3° amines Hinsberg Reagent is

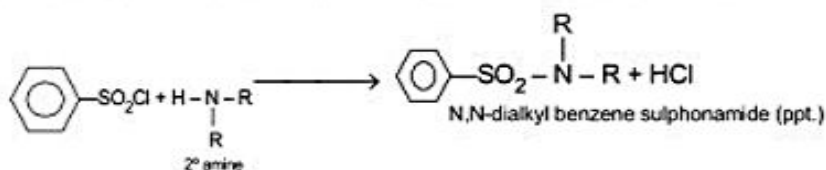
$\text{C}_6\text{H}_5\text{-SO}_2\text{-Cl}$ . (Benzene sulphonyl chloride)



(a) Primary amines form N-Alkyl benzene sulphonamide

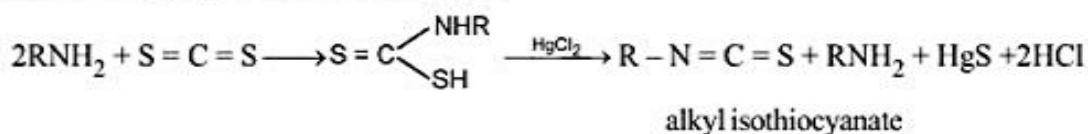


(b) Secondary amines form N, N-dialkyl benzene sulphonamide



(c) Tertiary amines do not react because they do not possess a replaceable Hydrogen atom.

**Hofmann Mustard oil reaction:** A 1° amine reacts with  $\text{CS}_2$  and then with  $\text{HgCl}_2$  to form iso thiocyanate having pungent smell of mustard oil.



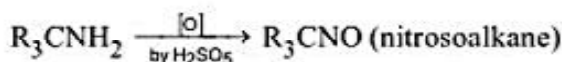
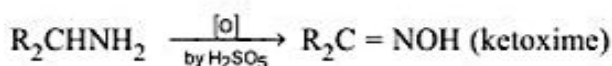
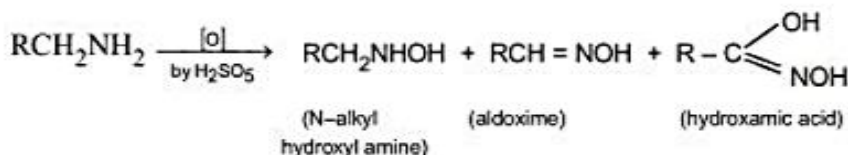


### Reaction with Nitrosyl chloride (TILDEN'S REAGENT)



### Reaction with Caro's acid [ $\text{H}_2\text{SO}_5$ ] :

With caro's acid, the oxidation products of primary amine are also dependent on the nature of the alkyl group present in the amine.

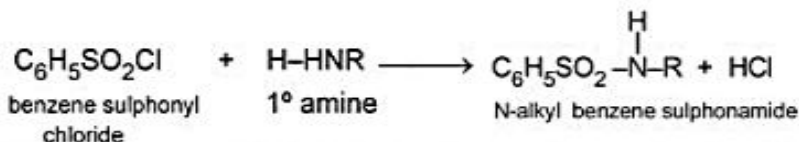


## SEPARATION OF MIXTURES OF AMINES

### Hinsberg method

This involves the treatment of the mixture with benzene sulphonyl chloride (Hinsberg Reagent) and KOH.

- (a) The primary amine forms N-alkyl benzene sulphonamide which forms a salt with KOH, which is soluble in water.

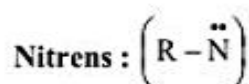


- (b) The secondary amine gives N, N- dialkyl benzene sulphonamide which is insoluble in KOH solution  
(c) The tertiary amine does not react at all.

**Hofmann method :** This involves the treatment of the mixture with diethyl oxalate.

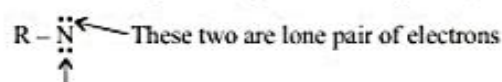
- (a) The primary amine forms a dialkyl oxamide, which is a solid  
(b) The secondary amine forms a dialkyl oxamic ester, which is an oily liquid.  
(c) The tertiary amine does not react at all.

**Fractional distillation :** The mixture of primary, secondary and tertiary amines, may be separated by fractional distillation because their B.P's. are quite different . This method is extensively used in industry.



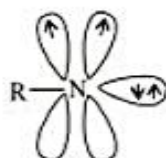
These are defined as 'the electron deficient species in which nitrogen has a sextet of electrons' (six electrons in the outermost shell). They are highly reactive and act as strong electrophiles as they need a pair of electrons to complete the octet. The parent species is  $\ddot{N} - H$ , known as nitrene or imidogene or azene or imine.

- (1) The nitrogen analogs of carbenes are called nitrenes.
- (2) There is possibility of two spin states for nitrenes depending on whether the two non-bonding electrons (the normal nitrogen lone pair remains paired) have their spins paired or parallel.



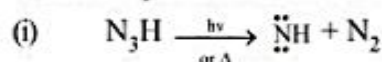
These two may be paired or unpaired

- (3) In general nitrenes obey Hunds rule and are ground state triplet with two degenerate sp-orbitals containing a single electron each.

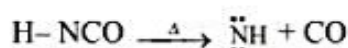


sp-Triplet nitrene

**Preparation of nitrene :** The simplest nitrene ( $\ddot{N}H$ ) is formed when hydrazoic acid ( $N_3H$ ) is irradiated with UV light in aromatic solvent.

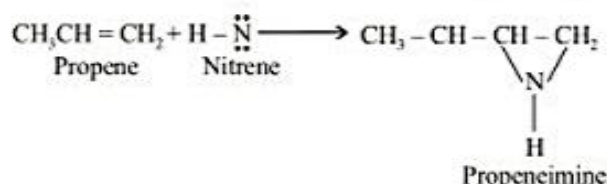


Similarly

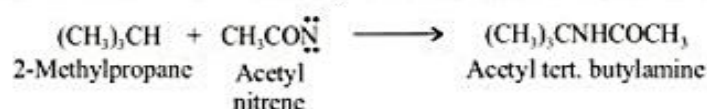


**Reactions - Nitrene** are highly reactive unstable compound and give the following

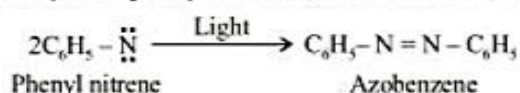
**Addition to alkenes :** Nitrenes add on alkenes to form corresponding alkeneimine, a cyclic product.



**Addition to alkanes :** Acetyl nitrene reacts with isobutane to form acetyl tert. butylamine.



Also photolysis of phenyl nitrene (on dimerization) forms azobenzene.

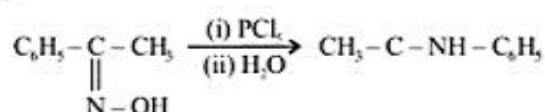


**Applications :** Nitrene have important synthetic applications particularly acyl nitrene ( $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\ddot{\text{N}}$ ), has been proposed as possible intermediate in the Hofmann, Curtius and Lossen rearrangements.

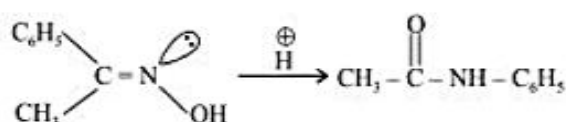
Name of Reaction	Reactant	Reagent	Intermediate	Product
Hofmann bromamide	Amide	$\text{Br}_2/\text{KOH}$	$\text{R}-\text{N}=\text{C}=\text{O}$	$\text{R}-\text{NH}_2$
Schmidt Reaction	Carboxylic acid	$\text{N}_3\text{H}/\text{H}^+$	$\text{R}-\text{N}=\text{C}=\text{O}$	$\text{R}-\text{NH}_2$
Lossen Rearrangement	Oxamic acid & Oxamic Ester	$\text{H}^+$ or $\text{OH}^-$	$\text{R}-\text{N}=\text{C}=\text{O}$	$\text{R}-\text{NH}_2$
Curtius Rearrangement	Acyl chloride	$\text{NaN}_3$	$\text{R}-\text{N}=\text{C}=\text{O}$	$\text{R}-\text{NH}_2$

### The beckmann Rearrangement

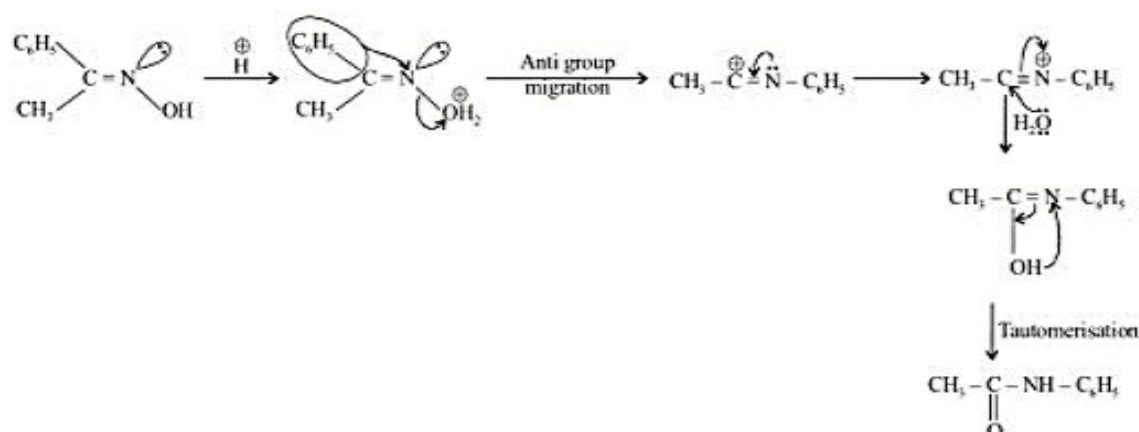
The acid catalysed conversion of ketoximes to N-substituted amides is called Beckmann rearrangement. Acid catalysts used are proton acids ( $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$ ,  $\text{H}_3\text{PO}_4$ ) and Lewis acids ( $\text{PCl}_5$ ,  $\text{SOCl}_2$ ,  $\text{PhSO}_2\text{Cl}$ ,  $\text{RCOCl}$ ,  $\text{SO}_3$ ,  $\text{BF}_3$  etc.)



**Example :**

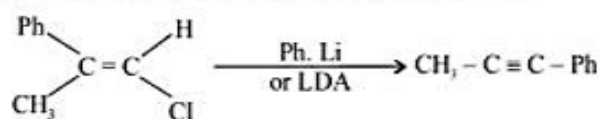


### Mechanism

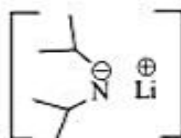
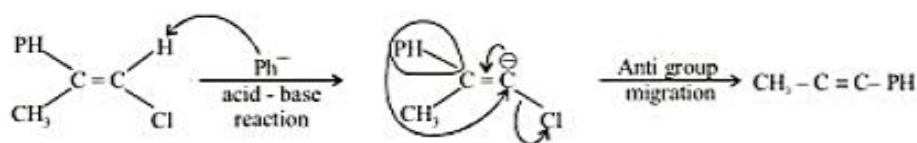


**Fritsch Reaction :**

Monohalogen derivatives of alkene in presence of strong base give the product containing carbon-carbon  $\equiv$  bond & known as Fritsch reaction.



Note : LDA is a very strong base.

**Mechanisms****CYANIDES, ISOCYANIDES, ALKYL NITRITES AND NITRO ALKANES****General Characteristics**

- (a) Compounds having the formula RCN are called alkyl cyanides or as nitriles of the acid which they produce on hydrolysis.
- (b) According to IUPAC system, cyanides are named as alkane nitriles, i.e., in the name of parent hydrocarbon 'nitrile' is suffixed. In naming the hydrocarbon part, carbon of the  $\text{—CN}$  group is also counted.

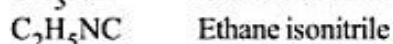
Formula	As cyanide	IUPAC name
$\text{CH}_3\text{CN}$	Methyl cyanide	Ethane nitrile
$\text{C}_2\text{H}_5\text{CN}$	Ethyl cyanide	Propane nitrile
$\text{C}_3\text{H}_7\text{CN}$	Propyl cyanide	Butane nitrile
$\text{C}_4\text{H}_9\text{CN}$	Butyl cyanide	Pentane nitrile

- (c) The compounds having the formula RNC are called isocyanide or isonitriles. The nomenclature of isocyanides is similar to cyanides.

Formula	As isocyanides (Common name)	IUPAC names
$\text{CH}_3\text{NC}$	Methyl isocyanide (Methyl isonitrile)	Methylcarbylamine (Carbylamino methane)
$\text{C}_2\text{H}_5\text{NC}$	Ethyl isocyanide (Ethyl isonitrile)	Ethyl carbylamine (Carbylamino ethane)
$\text{C}_3\text{H}_7\text{NC}$	Propyl isocyanide (Propyl isonitrile)	Propyl carbylamine (Carbylamino propane)



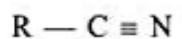
- (d) Isocyanides are also named as alkane isonitrile.



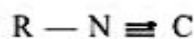
- (e) Hydrogen cyanide is known to exist as a tautomeric mixture. (Diad forms)



Hence, it forms two types of alkyl derivatives which are known as alkyl cyanides and alkyl isocyanides.



Alkyl cyanide

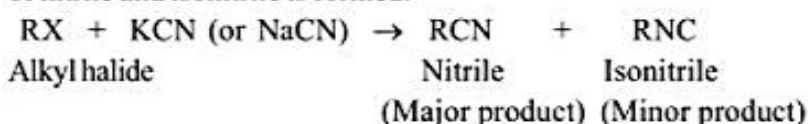


Alkyl isocyanide

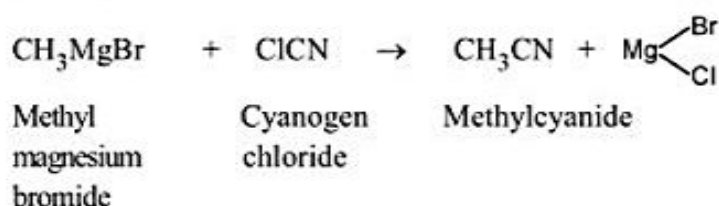
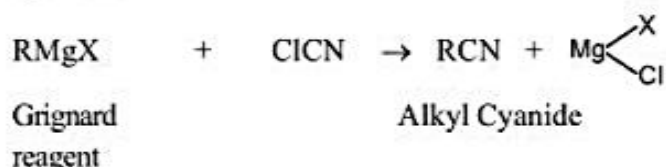
## ALKYL CYANIDES

### Methods of Preparation

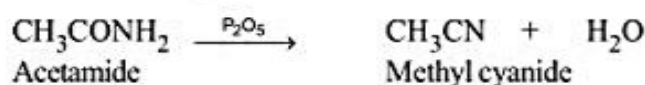
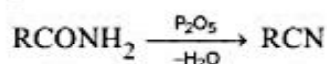
- (i) **From alkyl halides :** The alkyl cyanides are prepared by refluxing an alcoholic solution of an alkyl halide with potassium cyanide. The disadvantage of this method is that a mixture of nitrile and isonitrile is formed.



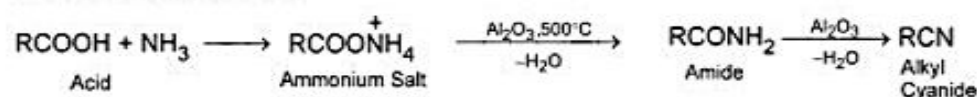
- (ii) **From Grignard reagent :** Grignard reagent reacts with cyanogen chloride to form alkyl cyanides.



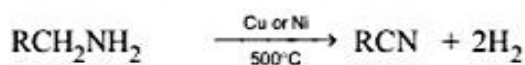
- (iii) **From acid amides :** Pure nitriles are obtained by dehydration of acid amides with phosphorus pentoxide. Amides are distilled with phosphorus pentoxide,  $\text{P}_2\text{O}_5$ .



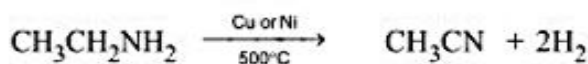
Industrially, alkyl cyanides are prepared by passing a mixture of carboxylic acid and ammonia over alumina at  $500^\circ\text{C}$ .



- (iv) **From primary amines :** Primary amines are dehydrogenated when passed over copper or nickel at high temperature to form alkyl cyanides. This is also a commercial method.



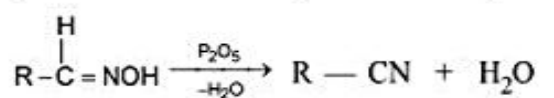
Primary amine



Ethylamine

Methyl cyanide

- (v) **From oximes :** Aldoximes are converted into alkyl cyanides when distilled with phosphorus pentoxide or acetic anhydride. The dehydration of aldoximes occurs.



Aldoxime

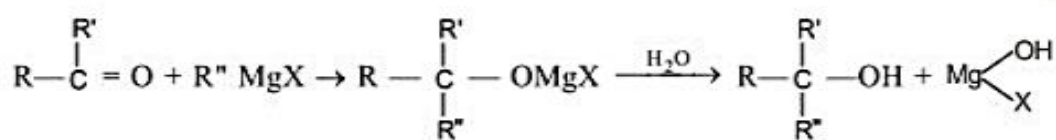
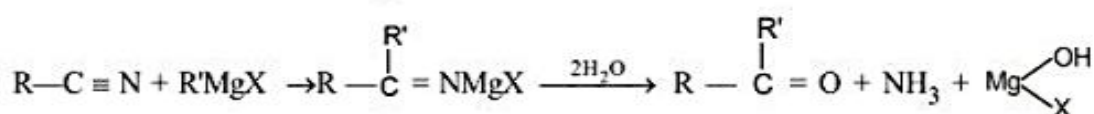
Alkyl cyanide

## PHYSICAL PROPERTIES

- Lower members containing upto 15 carbon atoms are liquids, while higher members of carbon atoms in the molecule.
- Alkyl cyanides are neutral substances with pleasant odour, similar to bitter almonds.
- They are soluble in water. The solubility decreases with the increase in number of carbon atoms in the molecule are solid.
- They are soluble in organic solvents.
- They are poisonous but less poisonous than HCN.

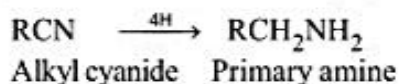
## CHEMICAL PROPERTIES

- (i) **Reaction with Grignard reagent :** With Grignard's reagent, an alkyl cyanide forms a ketone which further reacts to form a tertiary alcohol.



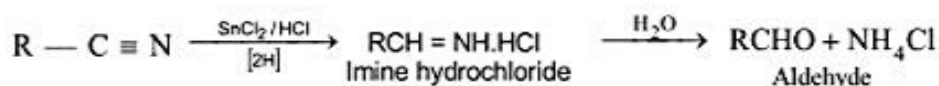
Tertiary alcohol

- (ii) **Reduction :** When reduced with hydrogen in presence of Pt or Ni, or  $\text{LiAlH}_4$  (Lithium aluminium hydride) or sodium and alcohol, alkyl cyanides yield primary amines.

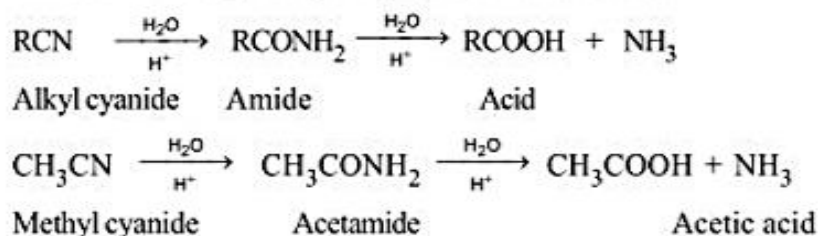


Alkyl cyanide    Primary amine

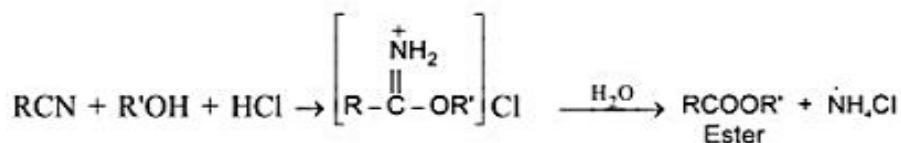
However, when a solution of alkyl cyanides in ether is reduced with stannous chloride and hydrochloric acid and then steam distilled, an aldehyde is formed (**Stephen's reaction**).



- (iii) **Hydrolysis :** Alkyl cyanides are hydrolysed by both acid and alkalies. On partial hydrolysis amides are formed while on complete hydrolysis acids are obtained.



- (iv) **Alcoholysis :** When an alkyl cyanide is refluxed with an anhydrous alcohol in presence of dry HCl, an imido ester is formed, which on hydrolysis with water forms ester.

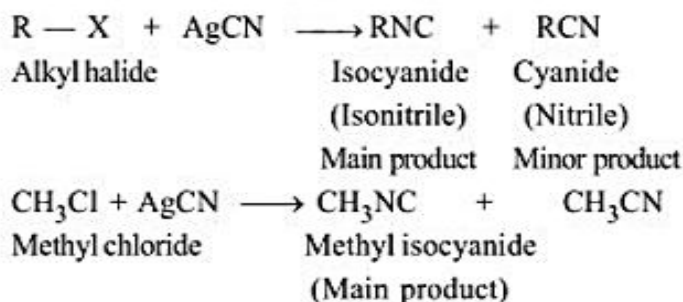


**Uses :** Alkyl cyanides are important intermediates in the laboratory synthesis of a large number of compounds like acids, amides, ester, amines, etc.

## ALKYL ISOCYANIDES

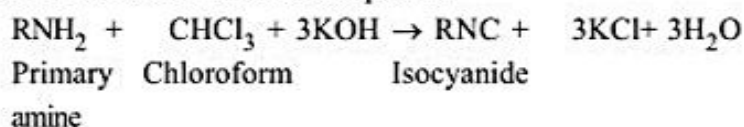
### Methods of Preparation

- (i) **From alkyl halides :** The isocyanides are prepared by refluxing an alkyl halide solution in alcohol with silver cyanide. The isonitrile is the main product but small amount of nitrile is also formed.



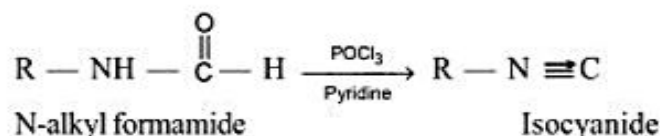
This method is, thus, suitable for preparing isocyanides.

- (ii) **From Primary Amines : (Carbylamine reaction) :** Alkyl isocyanides may be prepared by heating primary amines with chloroform and alcoholic potash.





- (iii) **From N-alkyl formamides** : N-alkyl formamides when dehydrated with  $\text{POCl}_3$  in presence of pyridine give isocyanides.

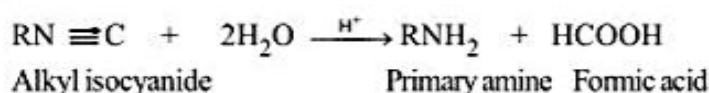


## PHYSICAL PROPERTIES

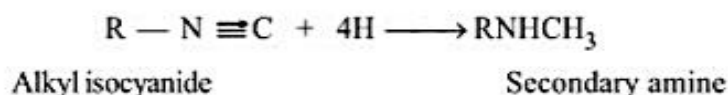
- (a) Alkyl isocyanides are colourless, unpleasant smelling liquids.
- (b) They are insoluble in water but freely soluble in organic solvents.
- (c) The boiling points of isonitriles are lower than corresponding alkyl cyanides.
- (d) Isonitriles are much more poisonous than isomeric cyanides.

## CHEMICAL PROPERTIES

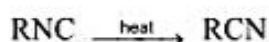
- (i) **Hydrolysis** : Alkyl isocyanides are hydrolysed by dilute mineral acids (but not by alkalies) to form primary amines.



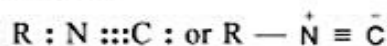
- (ii) **Reduction** : When reduced with nascent hydrogen or hydrogen in presence of nickel, isocyanides form secondary amines containing methyl as one of the alkyl groups.



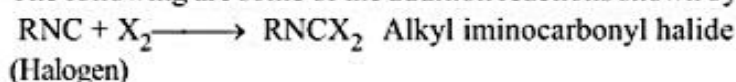
- (iii) **Action of heat** : When heated for sometime at  $250^\circ\text{C}$ , a small amount of isonitrile changes into isomeric nitrile.



- (iv) **Addition reaction** : Alkyl isocyanide give addition reactions due to presence of unshared electron pair on carbon atom.



The following are some of the addition reactions shown by alkyl isocyanides.





**Distinction between Ethyl Cyanide and Ethyl Isocyanide**

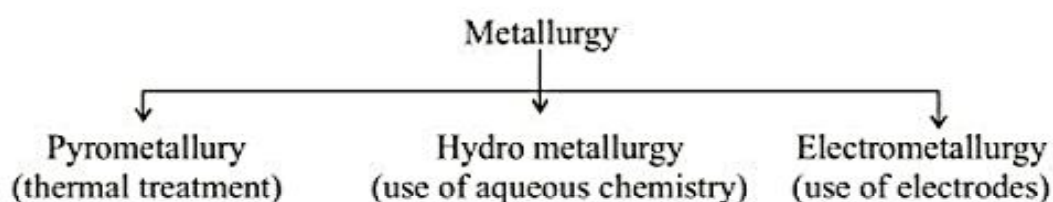
S.No.	Test	Ethyl Cyanide ( $C_2H_5CN$ )	Ethyl isocyanide ( $C_2H_5NC$ )
1	Odour	Not unpleasant	Extremely unpleasant
2	Solubility in water	Soluble	Insoluble
3	Hydrolysis	Yields propionic acid	Produces ethyl amine
4	Reduction	Gives propylamine (Primary amine)	Gives ethylmethylaniline (Secondary amine)
5	Heating at $250^\circ C$	No effect	Changes to ethyl cyanide

# METALLURGY

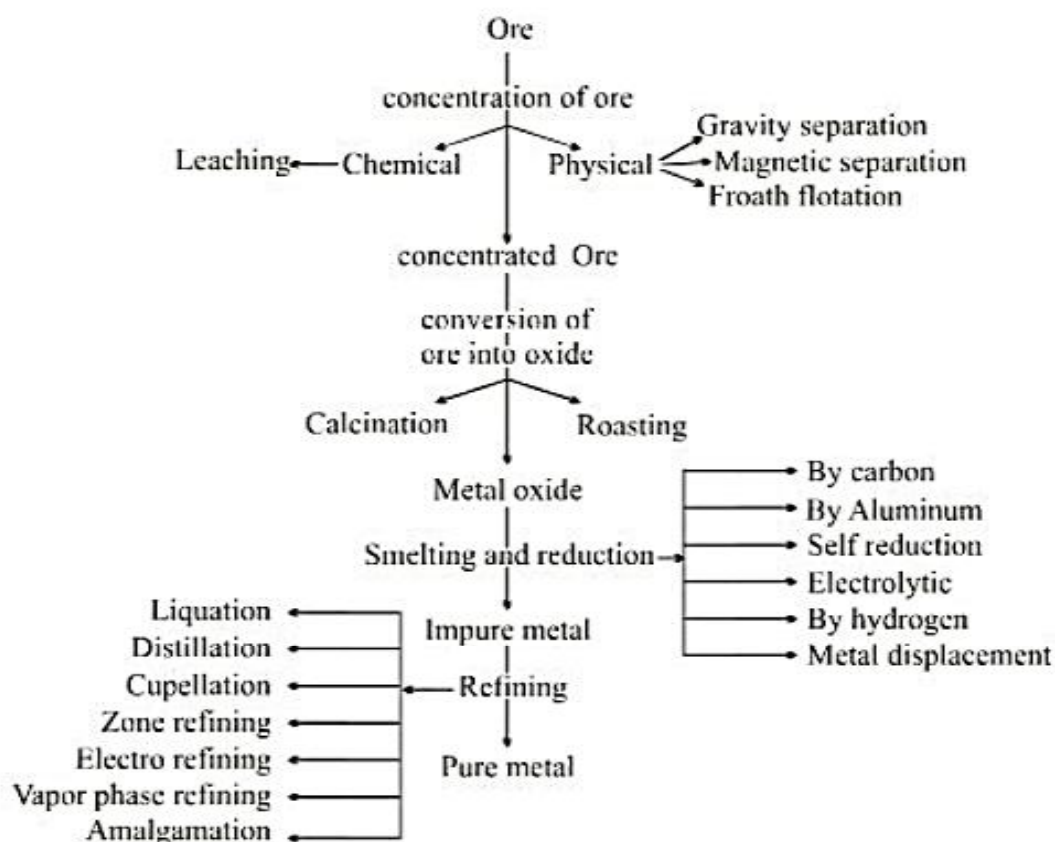
## INTRODUCTION

The process of extraction of metal from its ores in profitable manner is called metallurgy.

- (i) **Mineral** is a substance in which metal is present in either native state or combined state.
- (ii) **"Ore"** is the mineral form which the metal can be economically and conveniently extracted.
- (iii) **"Gangue or matrix"** is the non metallic impurities present in the ore.



## Steps involved in metallurgy



## COMMON STEPS INVOLVED IN METALLURGY

- Crushing and grinding (Pulverization)**

Operation in which size reduction of large lumps to small pieces followed by finely ground material is done by the use of crushers and grinders.

**Handpicking :** To pick up selective pieces of ores.

- Concentration (Dressing) of the ore**

Operation in which the removal of impurities (gangue) from ore by the following methods.

**Levigation or gravity separation :**

- This method is based on the difference in densities of the ore gangue particles.
- The powdered ore with gangue particles is introduced in the running stream of water.
- Lighter impurity particles washed off with water and heavier ore particles settle down at the bottom.  
Eg. Generally oxides & carbonate ores are concentrated by this method.

**Magnetic separation**

Ore and gangue are separated, if only one of them is having magnetic property.

Eg. In metallurgy of Fe .

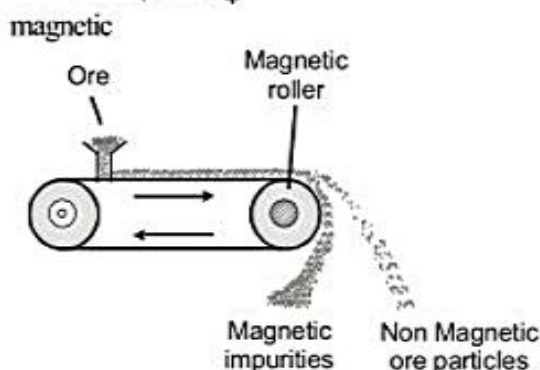
Ore  $\longrightarrow$  magnetic

impurity  $\longrightarrow$  non magnetic

In metallurgy of Sn (tin stone)

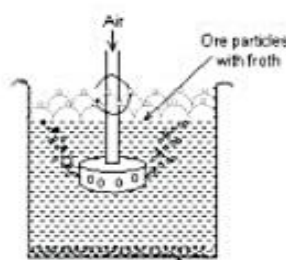
Ore  $\longrightarrow$  non magnetic ( $\text{SnO}_2$ )

impurity  $\longrightarrow$  wolframite ( $\text{FeWO}_4$ )



- Froath flotation process**

- It is employed for sulphide ores.
- It is based on the different wetting characteristics of the ore and gangue particles with water and oil.



- (iii) Usually ore particles are making as aerophilic & gangue particles as aerophobic by using different reagents.
- (iv) Ore particles raised to the surface along with air bubbles and collected at the surface where as gangue particles are wetted and settled down at the bottom of the tank.
- (v) Reagents used a frothing agents (pine oil), collectors (sodium ethyl xanthate and potassium ethyl xanthate), Activators (copper sulphate) and depressors (sodium cyanide, alkali).

\* **Collectors :**

These compounds adsorb themselves on polar groups to grains of ores and thus derive them on the surface to pass on into the forth e.g. sodium ethyl xanthate and potassium ethyl xanthate.

\* **Activators and depressants :**

These compounds activate or depress the floating property of one of the components of the ore and thus help in the separation of different minerals present in the same ore. Copper sulphate is an example of activator, while sodium and potassium cyanides are the examples of depressants e.g. Galena (PbS) is usually associated with sphalerite (ZnS) and pyrites (FeS<sub>2</sub>). Floatation is carried out in presence of potassium ethyl xanthate (collector) and sodium cyanide and alkali (depressants). The later compounds depress the flotation property of ZnS and FeS<sub>2</sub> particles and hence only PbS particles go into the forth when air is blown in. After the removal of galena, the process is repeated by adding copper sulphate (activator) which activates the floating character of ZnS particles and thus this time ZnS comes with the froath. The acidification of remaining slurry leads to the flotation of FeS<sub>2</sub>.

• **Leaching**

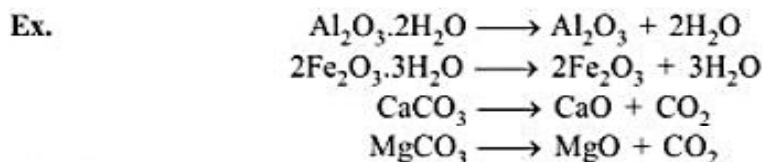
- (i) Chemical method of concentration.
- (ii) Selective dissolution of ore in strong reagents where as gangue particles are undissolved and gets separated. (Hydrometallurgy)
- (iii) Employed for concentrating ores of aluminium, silver, gold etc.

**Working of the concentrated ore**

• **Conversion of the concentrated ore into its oxide form**

(a) **Calcination :**

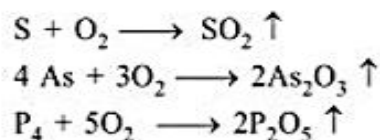
- (i) Ore is heated in absence of air to remove water or CO<sub>2</sub> from hydrated oxides or carbonates respectively.
- (ii) Process temperature is below the melting points of treated ores.
- (iii) During calcination moisture, volatile impurities are removed there by ore becomes porous.



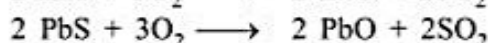
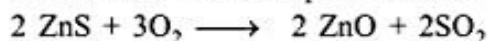
(b) **Roasting :**

- (i) Ore is heated strongly with other substances, usually with oxygen.
- (ii) Employed for sulphide ores.
- (iii) Process temperature is below the melting points of treated ore.
- (iv) Chemical conversion of ore is takes place.
- (v) Some of the impurities removed as volatile substances.



**Example :**

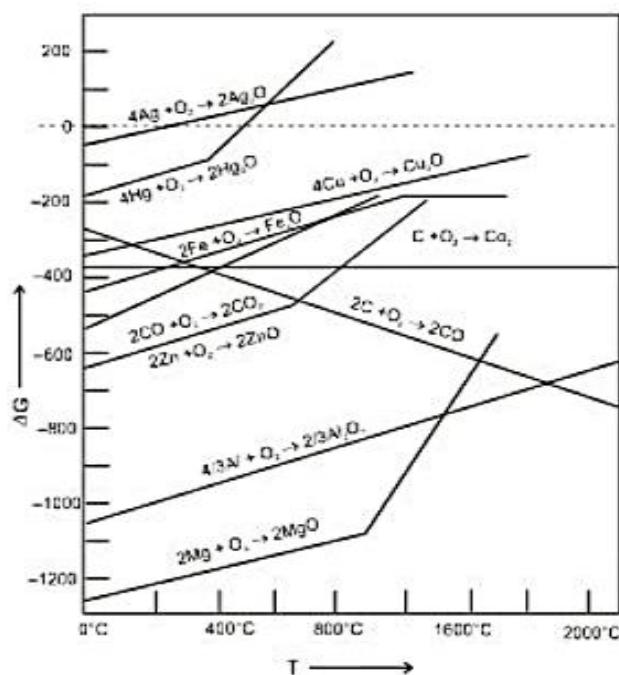
- (a) Conversion of metal sulphides into oxides.



- (b) Metal sulphides are converted into sulphates.

**Smelting**

- (i) Flux is added during smelting, which reduces the melting point of impurities to form an easily fusible substance called as '**slag**' and can be separated easily because of its lower density.
- (ii) Selection of flux depends upon nature of impurity present. Its impurity is acidic or basic flux is employed and vice versa.
- (iii) Smelting is usually carried out in blast furnaces or reverberatory furnace.

**Ellingham Diagram**

The changes in Gibbs energy that occur when one mole of oxygen is used may be plotted against temperature for a number of reactions of metals to form their oxides. Such a graph is shown in Figure below and is called an **Ellingham diagram** for oxides. Similarly, we can plot Ellingham diagrams for halides.

**The Ellingham diagram for oxides show the following important features :**

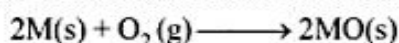
- (i) Ellingham diagram normally consist of plots of  $\Delta G^\circ$  vs T for the formation of oxides of elements, i.e. for the reaction.
- (ii) The graphs for metal oxide all slope upwards because the change in Gibbs energy becomes less negative with increase in temperature.
- (iii) Each plot follows a straight line unless there is some change in phase.
- (iv) When the temperature is increased, a point will be reached when the line crosses  $\Delta G = 0$  line. Below this temperature the  $\Delta_f G^\circ$  of oxide is negative and hence the oxide is stable. Above this temperature  $\Delta_f G^\circ$  of the oxide is positive and hence the oxide becomes unstable and decomposes on its own into metal and oxygen.

- **Conversion of the oxide to metallic form**

The roasted or calcined ore is converted into metallic form through reduction by using different reducing techniques which will depends upon the nature of the ore, some of the methods are mentioned below

**Thermodynamic Principles:**

Consider a reaction such as formation of an oxide.

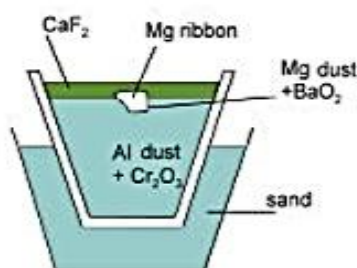


In this reaction, the random of the system decreases because gases have more random than solids. Hence,  $\Delta S$  for this reaction is negative. Thus, if temperature is increased then  $T\Delta S$  becomes more negative. Since  $T\Delta S$  is subtracted in equation,  $\Delta G$  becomes less negative. On the other hand, if  $\Delta S$  is positive, on increasing the temperature the value of  $\Delta G$  decreases and becomes more negative. For example, in the reaction,  $2C(s) + O_2(g) \longrightarrow 2CO(g)$ ,  $\Delta S$  is positive and  $\Delta G$  decrease and becomes more negative as the T increase.

**(a) Reduction by carbon**

The oxides of less electropositive metals like Pb, Zn, Fe, Sn, Cu etc. are reduced by strongly heating with coal or coke.

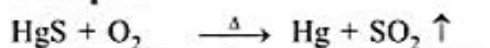
**(b) Reduction by aluminium (Alumino-thermic reduction)**



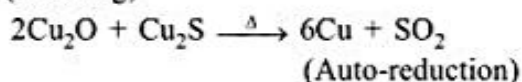
- (i) Aluminium acts as reducing agent due to its high electropositive nature.
- (ii) Oxides such as  $Cr_2O_3$ ,  $Mn_2O_4$  are reduced by this method
- (iii) The process is also known as “Gold Schmidt thermite process”.

**(c) Reduction by heating in air (Auto-reduction) /Self reduction**

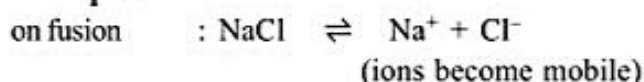
- (i) Employed for metals of less active such as Hg, Cu and Pb
- (ii) Due to unstable nature in the oxide form at high temperature, no reducing agent is required for their reduction..

**Example :**

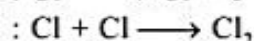
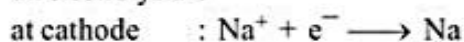
(Roasting)



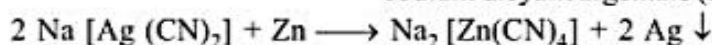
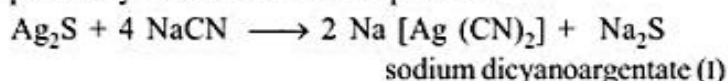
(Auto-reduction)

**(d) Electrolytic reduction (Electro-metallurgy)****(i)** Employed for highly electropositive metals such as Na, K, Ca, Mg etc.**(ii)** These metals are extracted by the electrolysis of their oxides, hydroxides or chlorides in fused state.**Example :**

on electrolysis :

**(iii)** Aluminium is obtained by the electrolysis of electrolyte which consists of mixture of alumina, cryolite and calcium fluoride (Hall-Herault process)**(e) Other method are following :****(i)** Reduction by carbon monoxide (employed for iron (iii) oxide)**(ii)** Reduction by water gas (employed for nickel oxide)**(iii)** Amalgamation method (employed for noble metals)

- Hydrometallurgy (Reduction by precipitation)**

**(i)** Process in which more electropositive metal displace less electropositive metals from salt solution.**(ii)** First the concentrated ore is dissolved in strong reagent and remove insoluble precipitates.**(iii)** Now the metal is precipitated by addition of more electropositive metal.**Example :** Silver sulphide dissolved in sodium cyanide which forms a soluble complex, then silver is precipitated by the addition of zinc powder.**Note :** This type of precipitation process is called **cementation**.**Refining or purification****(i)** The metals after reduction process consists of number of impurities like Si, P, slag, oxides, other metals etc.**(ii)** Removal of all these impurities to get pure metal is called as refining.**(iii)** Methods of refining are as under.

- Liquation**

**(i)** This is based on the principle of difference in melting points of metal and impurity.**(ii)** Employed for purification of low melting point metals like Pb, Sn etc.

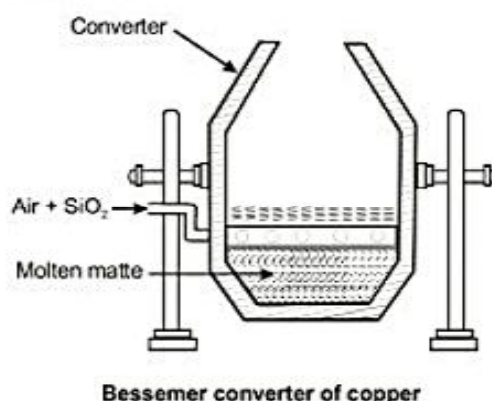


- **Distillation process**

- (i) This is based on difference in boiling points of metals and impurities.
- (ii) Employed for low boiling point metals like Zn, Hg etc.

- **Oxidation process**

- (i) This is a selective oxidation method.
- (ii) Used for refining those metals in which the impurities have greater tendency to get oxidised than the metals itself.
- (iii) The impurities converted into oxide & skimmed off from the metal.
- (iv) Various oxidation processes used for different metals bear different names, e.g., poling, puddling, bessemerisation and cupellation (for Ag).

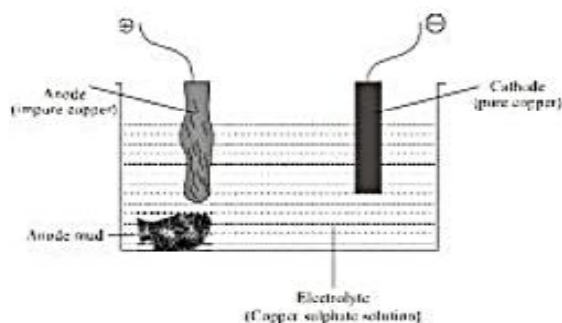


## CUPELLATION

The process in which a impure sample of metal (say Pb in Ag) is fused in a bone ash crucible (Cupel) on the hearth of furnace in the blast of air. The impurity (Pb) present is oxidized and blown away with air. Some PbO is absorbed by Cupel.

- **Electrorefining**

- (i) Employed for refining of highly electro positive metals like Al, Cu, Ag, Zn, Sn, Pb, Cr and Ni.
- (ii) Impure metal is made as anode, thin pure metal sheet is kept as cathode and the electrolysis comprising with soluble salt solution of the metal.
- (iii) On passing the electric current, pure metal from the anode dissolved and is deposited on the cathode.
- (iv) The soluble impurities goes into the solution (remains in the solution after the completion of refining) while the insoluble impurities settle down below the anode as “**anode mud**”

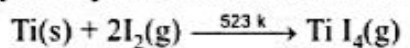


**Electrolytic refining of copper**

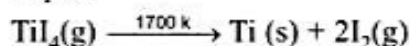


- **Van-Arkel process**

- (i) Employed to get metal in very pure form of small quantities.
- (ii) In this method, the metal is converted into a volatile unstable compound (e.g. iodide), and impurities are not affected during compound formation.
- (iii) The compound thus obtained is decomposed to get the pure metal.
- (iv) Employed for purification of metals like titanium and zirconium

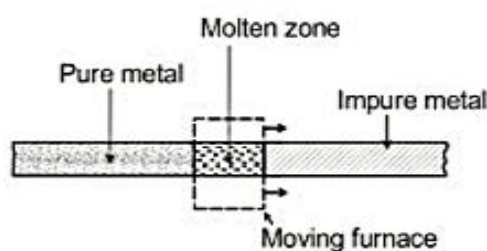


Impure



- **Zone refining**

- (i) Employed for metals which requires in very high purity like semi conductors.
- (ii) The method is based on the principle that an impure metal on solidification will deposit crystals of pure metal and the impurities will remain behind in the molten part of the metal.
- (iii) Used to purify the elements such as silicon, germanium.



**Zone refining**

**Amalgamation process :** Noble metals ores like Ag, Au, Pt in finely powdered state are mixed with water to form slurry. The slurry is then flown over Cu or brass plates coated with Hg arranged in slanting position. The metal particles forming amalgam with Hg are retained on these plates. The amalgam is scrapped off and then distilled in iron retorts where Hg distillates over leaving free metals. Hg vapours



- **Mond's process**

- (i) Nickel is purified by using CO gas. This involves the formation of nickel tetracarbonyl.



### Illustration

**Q.1** The ores that are concentrated by floatation method are –

- (A) Carbonates      (B) Sulphides      (C) Oxides      (D) Phosphates

**Ans.** (B)

**Sol.** In floatation process, the ore particles should be aerophilic in preference to gangue particles. Sulphide ores having this character.

**Q.2** Calcination is the process in which –

- (A) Heating the ore in presence of air      (B) Heating the ore in presence of sulphur  
(C) Heating the ore in absence of air      (D) Heating the ore in presence of chlorine

**Ans.** (C)

**Sol.** Calcination is the process in which moisture and volatile impurities are removed and process is carried in absence of air.

### Exercise

**Q.1** A substance which reacts with gangue to form fusible material is called –

- (A) Flux      (B) Catalyst      (C) Ore      (D) Slag

**Ans.** (A)

**Q.2** Which of the following is not a concentration technique –

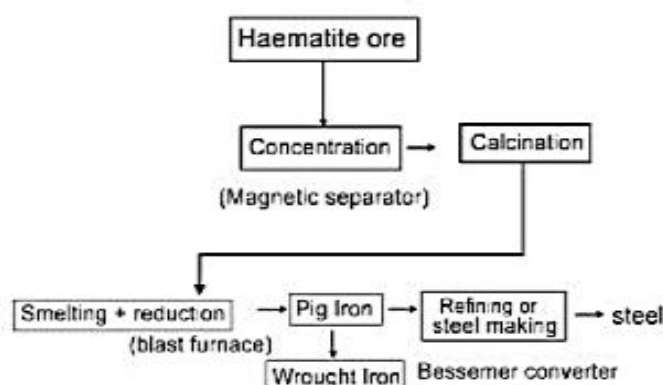
- (A) Levigation      (B) Froth floatation      (C) Leaching      (D) Calcination

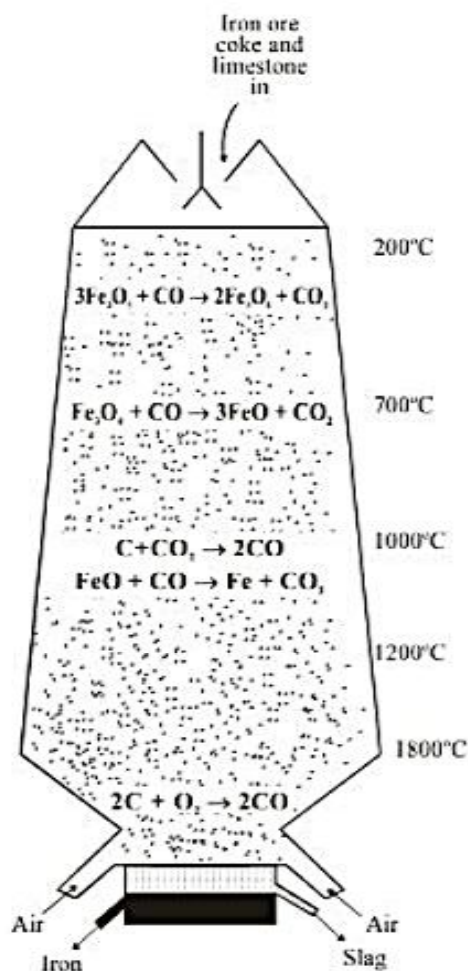
**Ans.** (D)

## EXTRACTION OF IRON

(a) **Ores :** Haematite –  $\text{Fe}_2\text{O}_3$  Limonite –  $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ; Siderite  $\text{FeCO}_3$ ; Magnetite –  $\text{Fe}_3\text{O}_4$ , Pyrite-  $\text{FeS}_2$ .

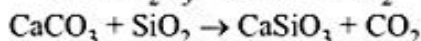
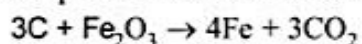
(b) **Process:**



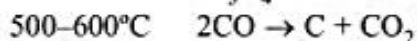
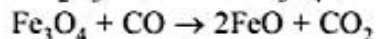
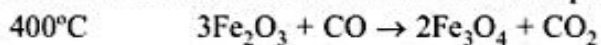


(c) **Reactions involved :**

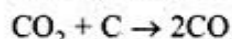
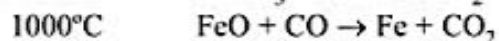
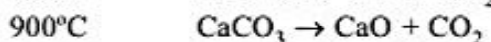
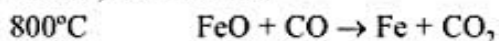
The overall process for the extraction of Fe is :



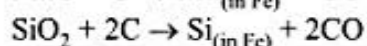
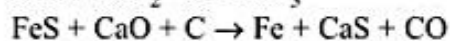
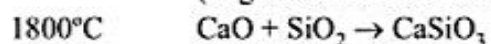
The reaction proceeds in several stages at different temperatures. Since the air passes through in a few seconds, The individual reactions do not reach equilibrium.



The C is deposited as soot and reduces FeO to Fe but it also reacts with the refractory lining of the furnace, and is harmful



(Together these two reactions appear to be  $\text{FeO} + \text{C} \rightarrow \text{Fe} + \text{CO}$ )



- (d) **Pig Iron** : C  $\approx$  3.1 – 4.5%, small amounts of Si, S, P ; hard and brittle, obtained from blast furnace  
 (e) **Wrought Iron** : C  $\approx$  0.15 – 0.28%, purest form ; malleable, fibrous

### Illustration

**Q.1** Magnetic separation is used for increasing concentration of the following –

- (A) Horn silver      (B) Calcite      (C) Haematite      (D) Magnesite

**Ans.** (C)

**Sol.** Haematite ore is having magnetic property, can be separated by magnetic separation

**Q.2** In blast furnace, iron oxide is reduced by –

- (A) Silica      (B) CO      (C) C      (D) lime stone

**Ans.** (B)

**Sol.**  $\text{FeO} + \text{CO} \longrightarrow \text{Fe} + \text{CO}_2$

### Exercise

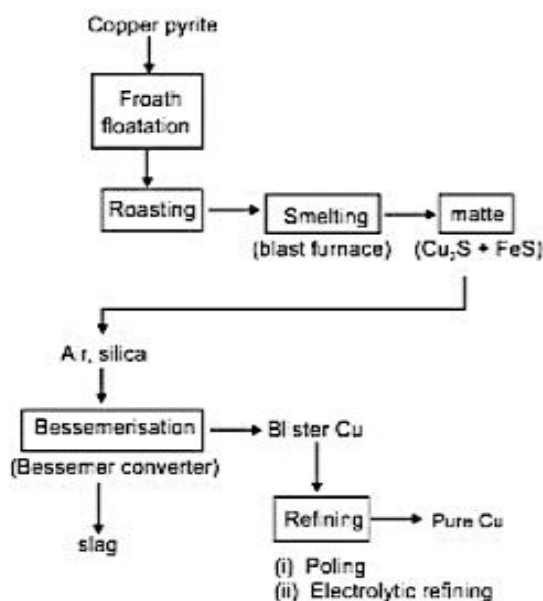
**Q.1** Steel consists of ..... percentage of carbon –

- (A) 3.1 – 4.5%      (B) 2.2 – 3.1%      (C) 0.15 – 0.28%      (D) 0.15 – 1.5%

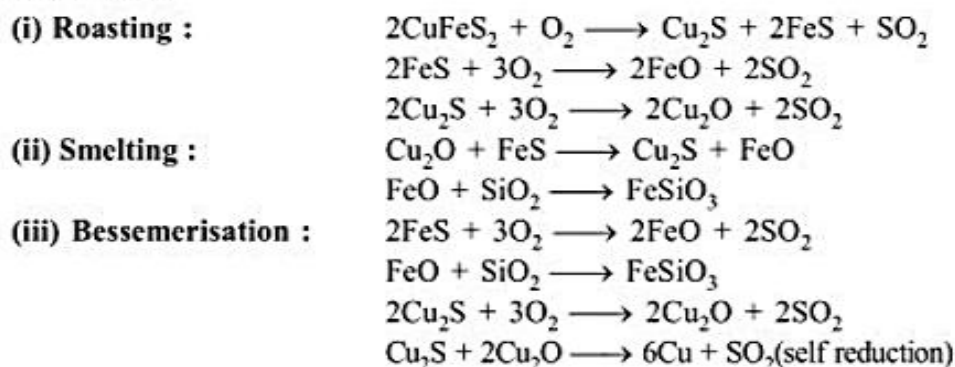
**Ans.** (D)

## EXTRACTION OF COPPER

- (a) **Ores** : Copper pyrites  $\text{CuFeS}_2$  ; Cuprite or ruby copper  $\text{Cu}_2\text{O}$  ; Copper glance  $\text{Cu}_2\text{S}$  ; Malachite  $\text{Cu}(\text{OH})_2 \cdot \text{CuCO}_3$  ; Azurite  $\text{Cu}(\text{OH})_2 \cdot 2\text{CuCO}_3$ .  
 (b) **Process**:





**(c) Reactions :**

**(iv) Poling :** Molten Cu is stirred with poles of green wood to reduce any copper oxide in Copper

**(v) Electrolytic refining :** Anode – impure Cu ; cathode – pure Cu ; electrolyte  $\text{CuSO}_4 + \text{H}_2\text{SO}_4$ .

**Note :** Low grade copper can be extracted by hydrometallurgical process also.

**Illustration**

**Q.1** In electrorefining of copper, some gold is deposited

- (A) as anode mud      (B) as cathode mud      (C) at the cathode      (D) in the electrolyte

**Ans.** (A)

**Sol.** In electrorefining of copper, impure copper is made as anode and a pure copper strip is made as cathode. A soluble copper salt is taken as electrolyte. On passing current, impurities like Fe, Zn, Ni, and Co dissolve in the solution and Au, Ag, etc. settle down as anode mud.

**Exercise**

**Q.1** Matte is obtained after this step –

- (A) Froath floatation      (B) Roasting      (C) Smelting      (D) Refining

**Ans.** (C)

**EXTRACTION OF ALUMINIUM****(a) Ores :**

(i) Oxides : Bauxite  $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$  (chief) ; Diaspore  $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$  ; Corundum  $\text{Al}_2\text{O}_3$ .

(ii) Silicates : Felspar  $\text{KAlSi}_3\text{O}_8$ ; Mica  $\text{K}_2\text{O} \cdot 3\text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ ; Kaolinite  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$

(iii) Fluorides : Cryolite  $\text{Na}_3\text{AlF}_6$

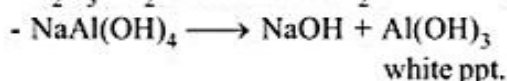
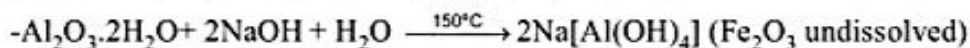
**(b) Process :**

(i) **Purification of Bauxite :**

(x) **Baeyer's Method**

If  $\text{Fe}_2\text{O}_3$  is major impurity - Red bauxite

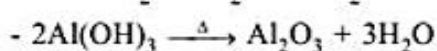
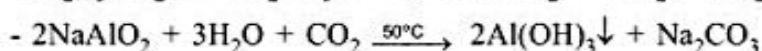
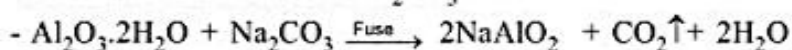
- ore is roasted to convert ferrous oxide to ferric oxide



(y) **Halls' method**

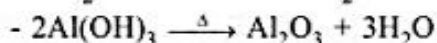
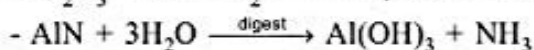
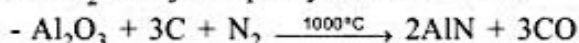
If  $\text{Fe}_2\text{O}_3$  is major impurity - Red bauxite

- bauxite ore is fused with  $\text{Na}_2\text{CO}_3$



(z) **Serpeck's method :**

(i) If  $\text{SiO}_2$  is major impurity - white bauxite



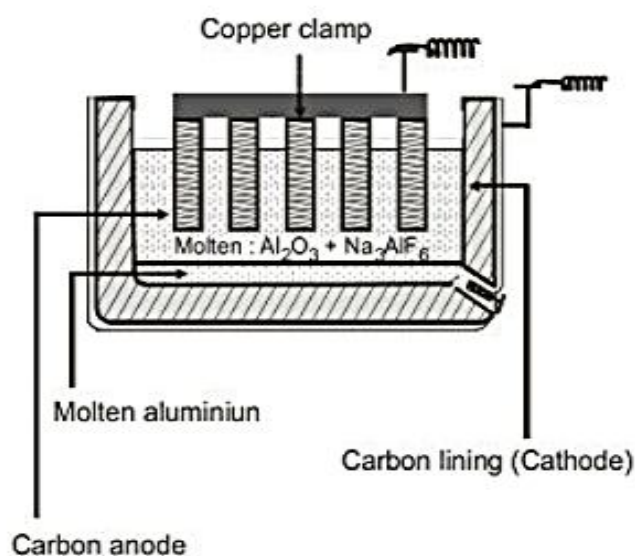
(ii) Electrolysis of fused Alumina.

Cathode : Iron-tank lined with carbon bricks

Anode : carbon

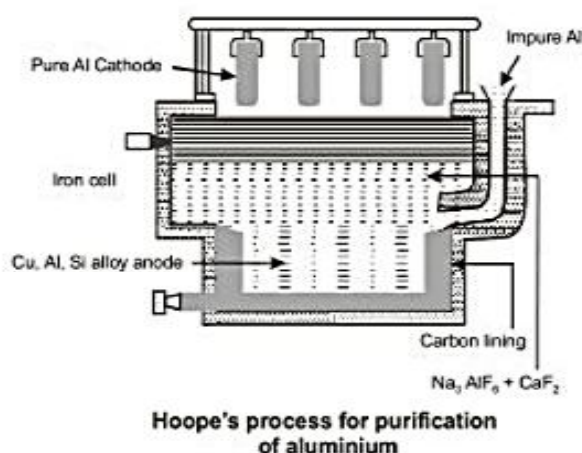
**Electrolyte :** Molten  $[\text{Al}_2\text{O}_3 (5\%) \text{ Na}_3\text{AlF}_6 (85\%) + \text{CaF}_2(5\%) + \text{AlF}_3(5\%) ]$

$\text{O}_2$  is liberated at anode and Al collects at the bottom.



**Hall Heroult process**

- (iii) Reactions :  $\text{Na}_3\text{AlF}_6 \longrightarrow 3\text{NaF} + \text{AlF}_3$   
 $\text{AlF}_3 \longrightarrow \text{Al}^{3+} + 3\text{F}^-$   
 At anode :  $\text{Al}_2\text{O}_3 + 6\text{F}^- \rightarrow 2\text{AlF}_3 + 3/2 \text{O}_2 + 6\text{e}^-$   
 At cathode :  $2\text{Al}^{3+} + 6\text{e}^- \longrightarrow 2\text{Al}$
- (iv) Electrolytic refining (Hoope's process), three layers process.  
 Cathode : carbon electrodes  
 anode : Fe tank lined with carbon bricks  
 Electrolyte :  $\text{Na}_3\text{AlF}_6 + \text{CaF}_2$



Bottom layer : Impure aluminium consists of Cu, Si etc. in molten state.

Middle layer : molten mixture of Fluorides of Na, Ba, Al and  $\text{Al}_2\text{O}_3$

Top layer : pure molten aluminium.

On passing the current, Al is deposited at cathode from the middle layer and an equivalent amount of Al from the bottom layer moves into the middle layer leaving behind the impurities.

### Illustration

**Q.1** Aluminium is obtained from  $\text{Al}_2\text{O}_3$  by this method –

- (A) Thermal reduction (B) Hydro metallurgical method  
 (C) Electrolytic reduction (D) Reduction by Iron.

**Ans.** (C)

**Sol.** For all metals with high electropositive nature, electrolytic reduction is best method.

### Exercise

**Q.1** If Bauxite consists of  $\text{SiO}_2$  as impurity, this process is employed –

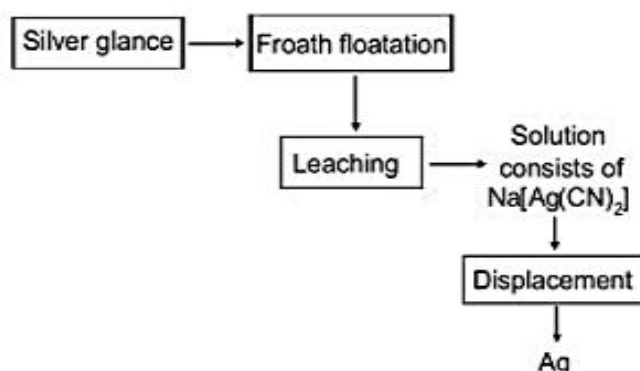
- (A) Hall's process (B) Baeyer's process (C) Hoope's process (D) serpeck's process

**Ans.** (D)

## EXTRACTION OF SILVER

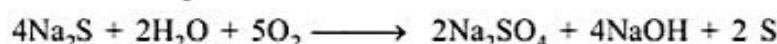
(a) **Ores :** Silver glance or argentite  $\text{Ag}_2\text{S}$ , Ruby silver  $\text{Ag}_2\text{S} \cdot \text{Sb}_2\text{S}_3$ , Horn silver  $\text{AgCl}$ .

(b) **Process :** Cyanidation or Mac-Arthur-Forrest cyanide process



(c) **Reactions (Leaching) :**

$\text{Ag}_2\text{S} + 4 \text{NaCN} \longrightarrow 2\text{Na}[\text{Ag}(\text{CN})_2] + \text{Na}_2\text{S}$ ; passing of air causes oxidation of  $\text{Na}_2\text{S}$ , thereby forward reaction takes place.



sodium argento cyanide

sodium zinc cyanide

The precipitated silver is separated and purified by fusion with borax or  $\text{KNO}_3$  to get pure silver.

Electrolytic refining: Anode : Impure Ag

cathode : Pure Ag

Electrolyte :  $\text{AgNO}_3(\text{aq.}) + \text{HNO}_3$ .

### Illustration

**Q.1** Which of the following processes is/are the examples of leaching:

(I) Mac Arthur forest process

(II) Hoop's process

(III) Baeyer's process

(IV) Allumino thermite process

Choose the correct code:

(A) I, II and III

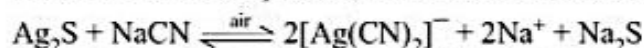
(B) I, III and IV

(C) I and III

(D) III only

**Ans.** (C)

**Sol.** (I) In Mac Arthur forest process, silver ore is leached out as  $[\text{Ag}(\text{CN})_2]^-$



(II) In Baeyer's process, alumina and  $\text{SiO}_2$  is leached out as  $[\text{Al}(\text{OH})_4]^-$  and  $\text{Na}_2\text{SiO}_3$  respectively.

(III) Hoop's process is used for purification of Aluminium.



**Exercise**

**Q.1** Leaching is preferred for which sulphide ore.

- (A) Galena (B) Argentite (C) Sphalerite (D) Cinnabar

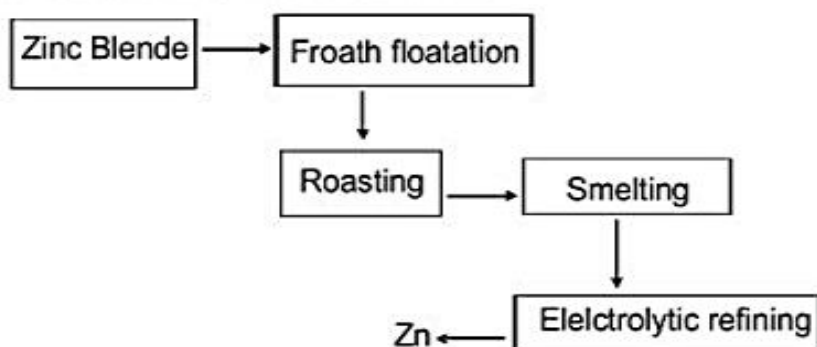
**Ans.** (B)

**EXTRACTION OF ZINC**

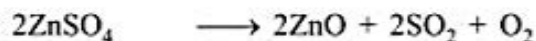
**Occurrence :** Zinc is usually found in the combined state although traces of the metal in the native state have been reported from Melbourne (Australia). Its chief ores are :

1. Zinc blende,  $\text{ZnS}$ .
2. Calamine or Sphalerite,  $\text{ZnCO}_3$
3. Zincite,  $\text{ZnO}$

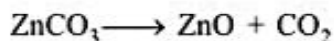
1. **Extraction process :** It involves the following steps :



2. **Roasting :**  
**Reactions:**



When the ore is calamine, it shall decompose into oxide with evolution of carbon dioxide (calcination is used).



For roasting, a reverberatory furnace may be used.

**Smelting**

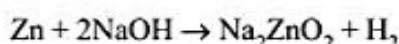
**Illustration**

**Q.1** Zn and Ag can be separated from each other by

- (A) distillation (B) heating with conc. NaOH  
(C) treating with dil.  $\text{HNO}_3$  (D) fractional crystallisation

**Ans.** (B, D)

**Sol.** Zinc is a volatile metal. Its boiling point is 1180K. It can be separated from silver by distillation. It can also be separated by heating with conc. NaOH solution in which Zn gets dissolved leaving Ag as such. The reaction is

**Exercise**

**Q.1** Calamine is concentrated by :

- (A) Magnetic Separation (B) Froath floatation  
(C) Cynide process (D) Gravity separation

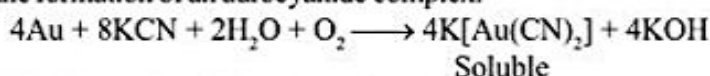
**Ans.** (D)

**EXTRACTION OF GOLD****Occurrence of Gold :**

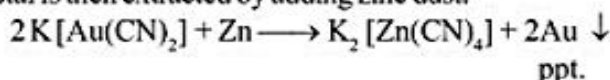
Gold is mainly found in native state either as vein gold, placer gold or alluvial gold. It is also present to a small extent in the combined state as sulphide, telluride and arsenosulphide. Some important ores of gold are :

(i) Calaverite,  $\text{AuTe}_2$  (ii) Sylvanite,  $\text{AuAgTe}_2$  and (iii) Bismuth aurite,  $\text{BiAu}_2$

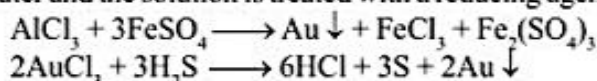
- (i) **Mac-Arthur-Forest Cyanide process :** The powdered gold ore, after concentration by Forth-floatation process, is roasted to remove easily oxidisable impurities of tellurium, arsenic and sulphur. The roasted ore is then treated with a dilute solution of KCN in presence of atmospheric oxygen when gold dissolves due to the formation of an aurocyanide complex.



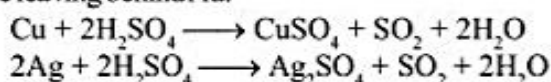
The metal is then extracted by adding zinc dust.



- (ii) **Plattner's chlorine process :** The roasted ore is moistened with water and placed in wooden vats with false perforated bottoms. It is saturated with current of chlorine, gold chloride thus formed is leached with water and the solution is treated with a reducing agent such as  $\text{FeSO}_4$  or  $\text{H}_2\text{S}$  to precipitate gold.



The impure gold thus obtained contains imparities of Ag and Cu. The removal of Ag and Cu from gold is called parting. This is done by heating impure gold with conc.  $\text{H}_2\text{SO}_4$  (or  $\text{HNO}_3$ ) when Ag and Cu dissolve leaving behind Au.

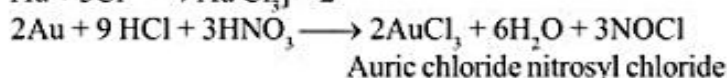
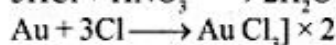


**Properties of gold :**

Gold is a yellow, soft and heavy metal. Gold and Ag are called noble metals since they are not attacked by atmospheric oxygen. However, Ag gets tarnished when exposed to air containing traces of  $\text{H}_2\text{S}$ . Gold is malleable, ductile and a good conductor of heat and electricity. Pure gold is soft. It is alloyed with Ag or Cu for making jewellery. Purity of gold is expressed in terms of carats. Pure gold is 24 carats. Gold '14 carats' means that it is an alloy of gold which contains 14 parts by weight of pure gold and 10 parts of copper per 24 parts by weight of the alloy. Thus the percentage of gold in "14 carats" of gold is =

$$\frac{100}{24} \times 14 = 58.3\%$$

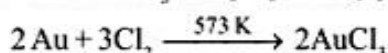
Most of the jewellery is made from 22 carat gold (91.66% pure gold). Gold is quite inert. It does not react with oxygen, water and acids but dissolves in aqua regia (3 parts concentrated  $\text{HCl}$  + 1 part concentrated  $\text{HNO}_3$ )

**Oxidation states of gold :**

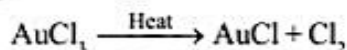
The principal oxidation states of gold are +1 and +3 though +1 state is more stable than +3

**Compounds of gold :**

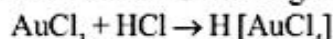
- (1) Auric chloride  $\text{AuCl}_3$ . It is prepared by passing dry  $\text{Cl}_2$  over finely divided gold powder at 573 K



It is a red coloured crystalline solid soluble in water and decomposes on heating to give gold (I) chloride and  $\text{Cl}_2$ .



It dissolved in conc.  $\text{HCl}$  forming chloroauric acid



Chloroauric acid is used in photography for toning silver prints and as an antidote for snake poisoning.

- (2) Aurous sulphide,  $\text{Au}_2\text{S}$ . It is prepared when  $\text{H}_2\text{S}$  is passed through an acidified solution of potassium aurocyanide,  $\text{K}[\text{Au}(\text{CN})_2]$



It is dark brown solid, not attacked by dilute mineral acids and hence is probably the most stable gold (I) compound

**Illustration**

- Q.1** Which of the following metals can not be extracted by self reduction?

(A) Au                      (B) Hg                      (C) Cu                      (D) Pb

**Ans.** (A)

**Sol.** Hg, Cu and Pb metals can be extracted by self reduction from their respective sulphide ores.

**Exercise**

- Q.1** Which of the following ore of the metal(s) is / are concentrated by leaching method

(A) Al                      (B) Fe                      (C) Au                      (D) Ag

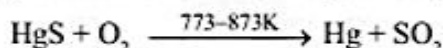
**Ans.** (A, C, D)



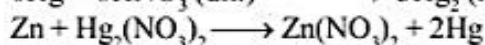
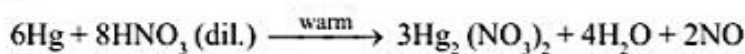
## EXTRACTION OF MERCURY

### Occurrence and extraction of mercury :

Cinnabar (HgS) is the only important ore of Hg. It is concentrated by froth floatation method and mercury is extracted from this ore by heating it in air at 773–873 K (auto reduction)



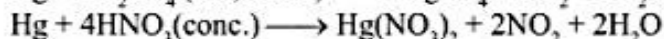
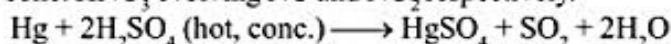
The mercury vapours thus obtained are condensed to give liquid metal. Hg thus obtained contains impurities of Zn, Sn and Pb. These are removed by treating the impure metal with dil.  $\text{HNO}_3$ . Mercurous nitrate,  $\text{Hg}_2(\text{NO}_3)_2$  thus formed reacts with metals present as impurities forming their nitrates which pass into solution leaving behind pure mercury. However, it is best purified by distillation under reduced pressure.



Similar reaction is given by Pb and Sn.

### Properties of mercury :

Mercury is less reactive than Zn. It is liquid at room temperature and has low thermal and electrical conductivity. Mercury forms dimeric mercury (II) ion,  $\text{Hg}_2^{+2}$  in which the two Hg atoms are bonded by a covalent bond. It is easily oxidised to HgO at about its boiling point. Hg does not react with dil. HCl or dil.  $\text{H}_2\text{SO}_4$  but reacts with hot concentrated  $\text{H}_2\text{SO}_4$  to form  $\text{HgSO}_4$ . It, however, reacts with both warm dil and conc.  $\text{HNO}_3$  evolving NO and  $\text{NO}_2$  respectively.



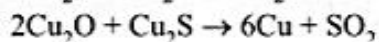
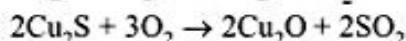
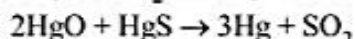
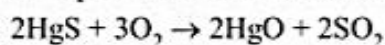
### Illustration

**Q.1** Auto reduction process is used in the extraction of

- (A) Cu and Hg      (B) Zn and Hg      (C) Cu and Mg      (D) Fe and Pb

**Ans.** (A)

**Sol.** Auto reduction takes place in the case of Cu and Hg. The reactions are as follows:



### Exercise

**Q.1** To obtain silver from silver amalgam it is heated in vessel which is made of

- (A) Cu      (B) Fe      (C) Ni      (D) Zn

**Ans.** (B)



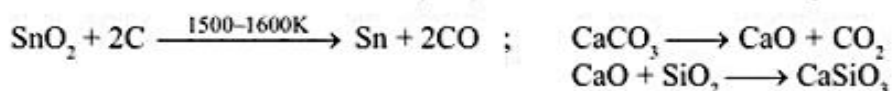
## EXTRACTION OF TIN

### Occurrence of tin :

Tin does not occur in nature in the native state. Its chief ore is cassiterite or tin stone ( $\text{SnO}_2$ ).

### Extraction of tin from tin stone :

The ore is crushed, washed and concentrated magnetically to remove magnetic impurities of tungstate of iron (wolframite,  $\text{FeWO}_4$ ) and manganese. The concentrated ore is roasted to remove sulphur and arsenic as their oxides. The roasted ore is then subjected to smelting i.e. ore is mixed with anthracite (coke) in the ratio 1 : 4 and little limestone (flux) and heated in a reverberatory furnace.

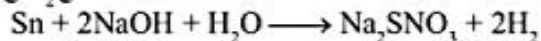


The molten metal is tapped out from the bottom of the furnace and cast into blocks. The tin thus obtained is called block tin and contains impurities of Fe, Pb and Cu etc. The crude metal is finally refined by either liquation, poling or electro-refining.

In electro refining, impure metal is made the anode while a sheet of pure metal acts as the cathode. The electrolyte consists of stannous sulphate  $\text{SnSO}_4$  containing little  $\text{H}_2\text{SO}_4$  and hydrofluosilicic acid ( $\text{H}_2\text{SiF}_6$ ). On passing current, tin dissolves from the anode and passes into the electrolyte while an equivalent amount of tin from the electrolyte gets deposited on the cathode.

### Properties of tin :

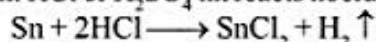
It is a soft white metal, malleable and ductile and can be rolled into sheets and foils. When heated in air, it forms  $\text{SnO}_2$ , with S it forms  $\text{SnS}_2$  and with  $\text{Cl}_2$  it gives  $\text{SnCl}_4$ . It dissolves in hot concentrated alkalis evolving  $\text{H}_2$  gas



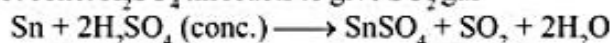
and reacts with  $\text{HNO}_3$  to give metastannic acid ( $\text{H}_2\text{SnO}_3$ )



With dil.  $\text{HCl}$  or  $\text{H}_2\text{SO}_4$  tin reacts liberating  $\text{H}_2$  gas



With hot conc.  $\text{H}_2\text{SO}_4$  tin reacts to give  $\text{SO}_2$  gas



Tin is widely used for plating iron and brass vessels to resist corrosion. Tin foils are also used for wrapping cigarettes and making food containers.

### Illustration

**Q.1** A tin ore ( $\text{SnO}_2$ ) contains  $\text{FeCrO}_4$  as impurity. It can be concentrated by

- |                          |                        |
|--------------------------|------------------------|
| (A) magnetic separation  | (B) froth floatation   |
| (C) electrostatic method | (D) gravity separation |

**Ans.** (A)

**Sol.**  $\text{FeCrO}_4$  is magnetic material. Obviously, it can be separated from tin ore ( $\text{SnO}_2$ ) which is non-magnetic by magnetic separation method.

---

**Exercise**


---

**Q.1** Cassiterite is concentrated by:

- |                |                                |
|----------------|--------------------------------|
| (A) Levigation | (B) Electromagnetic separation |
| (C) Floatation | (D) Liquefaction               |

**Ans.** (B)

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## EXTRACTION OF LEAD

### Occurrence of lead :

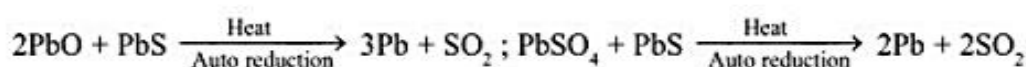
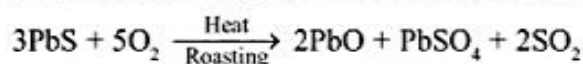
Lead does not occur in the free state. The important ores of lead are :

- (i) Galena (PbS)      (ii) Anglesite (PbSO<sub>4</sub>) and      (iii) Cerussite (PbCO<sub>3</sub>).

### Extraction of lead :

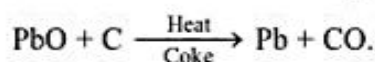
**(i) Self reduction process :**

Galena, after concentration by Froth-floatation process, is roasted in air to form PbO and PbSO<sub>4</sub>. The unchanged galena then brings about the reduction of PbO and PbSO<sub>4</sub> to Pb metal (auto reduction).



**(ii) Carbon reduction process :**

The roasted ore is reduced to metal by heating with coke.

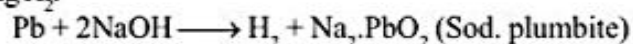


The metal obtained by above methods contain Ag, Cu, Fe, Sn and Sb as impurities. It is refined by either liquation, softening, desilverisation or electrolytic refining processes.

In electrolytic refining the electrolyte taken consists of a solution of lead fluorosilicate (PbSiF<sub>6</sub>) and hydrofluosilicic acid (H<sub>2</sub>SiF<sub>6</sub>) with a little gelatin.

### Properties of lead :

Lead is a bluish grey lustrous metal but when exposed to air, it acquires dull appearance due to the forming of a thin layer of Pb(OH)<sub>2</sub> and PbCO<sub>3</sub> on its surface. It dissolves in hot concentrated alkali evolving H<sub>2</sub>.



Other reactions with acids, S, Cl<sub>2</sub> are similar to those of Sn

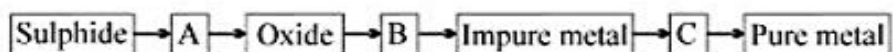
Lead forms two series of compounds i.e. Pb (II) and Pb(IV) compounds but Pb(II) compounds are more stable than Pb (IV) compounds. Pb (II) compounds are essentially ionic while Pb (IV) compounds are covalent in nature.

Lead used for making cable coverings, bullet shots, lead accumulators, tetraethyl lead (antiknocking agent) and a number of pigments such as red lead (Pb<sub>3</sub>O<sub>4</sub>); white lead [2Pb(OH)<sub>2</sub>.PbCO<sub>3</sub>], chrome yellow (PbCrO<sub>4</sub>) and chrome red (PbO.PbCrO<sub>4</sub>).

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**Illustration**

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**Q.1** Step C (refining) involved in purification of Pb metal

- (A) Distillation      (B) Bessemerization      (C) Cupellation      (D) Electrolytic refining

**Ans.** (D)

**Sol.** Sulphide ore  $\xrightarrow{\text{Roasting}}$  oxide  $\xrightarrow{\text{Auto Reduction}}$  Impure metal

---

**Exercise**

---

**Q.1** When ZnS and PbS minerals are present together, then NaCN is added to separate them in the froth floatation process as a depressant, because

- (A)  $\text{Pb}(\text{CN})_2$  is precipitated while no effect on ZnS  
(B) ZnS forms soluble complex  $\text{Na}_2[\text{Zn}(\text{CN})_4]$   
(C) PbS forms soluble complex  $\text{Na}_2[\text{Pb}(\text{CN})_4]$   
(D) They cannot be separated by adding NaCN.

**Ans.** (B)

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## SOLVED EXAMPLES

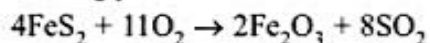
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**Q.1** Heating of pyrites in air for oxidation of sulphur is called

- (A) roasting                      (B) smelting                      (C) calcinator                      (D) slagging

**Ans.** (A)

**Sol.** Sulphide ores are strongly heated to convert them into oxides and this is called roasting.

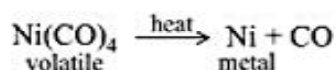


**Q.2** One of the following metals forms a volatile compound and this property is taken advantage of its extraction. The metal is

- (A) iron                      (B) nickel                      (C) cobalt                      (D) tungsten

**Ans.** (B)

**Sol.** Nickel combines with CO to form volatile  $\text{Ni}(\text{CO})_4$  (nickel carbonyl) which decomposes to give pure Ni metal and CO on heating.



**Q.3** Which of the following is not used for extraction of Aluminium –

- (A) Van arkel process                      (B) Serpeck's process  
(C) Baeyer's process                      (D) Hall-Heroult's process

**Ans.** (A)

**Sol.** Van Arkel process is one the refining process to get very pure metal. In this process the impure metal is converted into volatile Iodides, which are again dissociated to get pure metal.

**Q.4** Heating an ore in the absence of air below its melting point is called:

- (A) leaching                      (B) roasting                      (C) smelting                      (D) calcination

**Ans.** (D)

**Sol.** Roasting is heating in presence of air.

**Q.5** Zinc blende on roasting in air gives –

- (A) Zinc carbonate    (B)  $\text{SO}_2$  and ZnO    (C) ZnS and  $\text{ZnSO}_4$     (D)  $\text{CO}_2$  and ZnO

**Ans.** (B)

**Sol.**  $\text{ZnS} + \text{O}_2 \longrightarrow \text{ZnO} + \text{SO}_2$

**Q.6** Reagent used in cyanide process is –

- (A) NaOH                      (B) NaCN                      (C)  $\text{Na}_2\text{CO}_3$                       (D)  $\text{NaNO}_3$

**Ans.** (B)

**Sol.** It is used to concentrate gold & silver

**Q.7** In alumino-thermite process, aluminium is used as:

- (A) Oxidising agent    (B) Flux                      (C) Reducing agent    (D) Solder

**Ans.** (C)

**Sol.** Al is used to reduce oxide of Cr & Mn.

---



**Q.8** Which of the following is not a concentration technique  
 (A) Levigation (B) Froth floatation (C) Leaching (D) Calcination

**Ans.** (D)

**Sol.** In calcination, volatile impurities are removed by heating concentrated ore in Reverberatory furnace.

**Q.9** Cassiterite is an ore of :  
 (A) Mn (B) Ni (C) Sb (D) Sn

**Ans.** (D)

**Sol.** Cassiterite is  $\text{SnO}_2$

**Q.10** Cassiterite is concentrated by :  
 (A) Levigation (B) Electromagnetic separation  
 (C) Floatation (D) Liquefaction

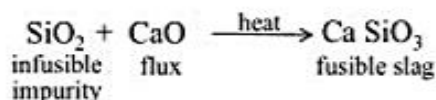
**Ans.** (B)

**Sol.** Its contain magnetic (wolframite) impurities.

**Q.11** In metallurgy, flux is a substance that is used to convert  
 (A) infusible impurities to fusible material (B) fusible impurities to infusible impurities  
 (C) soluble impurities to insoluble impurities (D) mineral into silicate

**Ans.** (A)

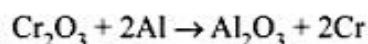
**Sol.** Flux converts infusible impurities to fusible material



**Q.12** Chromium is obtained by reducing purified chromite ore with  
 (A) red-hot coke (B) gaseous hydrogen (C) aluminium powder (D) carbon monoxide

**Ans.** (C)

**Sol.** Chromite ore ( $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ ) is first converted into free  $\text{Cr}_2\text{O}_3$ . It is then reduced by Al to pure chromium metal.



## p-BLOCK ELEMENTS-II

### NITROGEN FAMILY

#### GROUP 15 ELEMENTS (NITROGEN FAMILY)

The elements are : N, P [ Non metal], As [ Metalloid], Sb, Bi [Metal]

The General electronic configuration is [noble gas]  $ns^2 np^3$

#### (I) Atomic and Physical properties

(1) **Atomic and Ionic radii** : Covalent radius :  $N < P < As < Sb < Bi$

(2) **Ionization enthalpies** :  $N > P > As > Sb > Bi$  ( $IE_1$  values)

(3) **Electronegativity** :  $N > P > As > Sb = Bi$

(4) **Metallic Character** :  $\frac{N < P}{\text{Non metal}} \quad \frac{As < Sb < Bi}{\text{Metalloid Metals}}$

#### (5) Catenation

- \* The group 15 elements also show catenation property but to much smaller extent than carbon. For example hydrazine ( $H_2NNH_2$ ) has two N atoms bonded together  $HN_3$  has three N atoms.



- \* Among group 15 elements P has the maximum tendency for catenation forming cyclic as well as open chain compounds consisting of many phosphorous atoms.

$P_2H_4$  has two P atoms bonded together the lesser tendency of elements of group 15 to show catenation in comparison to carbon is their low dissociation enthalpies.

C – C	353.3 kJ /mole
N – N	16.8 kJ / mole
P – P	201.6 kJ / mole
As – As	147.4 kJ / mole

#### (6) Valency and Oxidation Number :

(a) Gen. configuration :  $ns^2 np^3$

Valency = 3

O.S. = - 3, + 3, + 5

P show O.S. = - 3, + 3

(b) P has two sleeping valency.

(c) **Sleeping Valency** : These electron of valency shell which does not take part in bonding.

(d) P in excited state show + 5 O.S.

So Hybridisation =  $sp^3d$

Shape = Trigonal by pyramidal.

(e) P, As, Sb Show 3 & 5 both O.S.

N only 3, absence of d-orbital

Bi only 3, because of inert pair effect

**(7) Reactivity :**

- (a)  $\downarrow$  Decreases  $\therefore$  E.N. Decrease  
 (b) Least reactive in V group is N {due to triple bond formation of Bond Energy ( $\uparrow$ )  
 (c) Max. Reactive in V group is P.  
 (d) Order  $P > As > Sb > Bi > N$

**(8) Allotropic Forms :** Except N and Bi all other elements of this group show allotropy.

Phosphorous : White, Black and Red

Arsenic : Yellow or Grey

Antimony : Yellow or Silvery grey.

\* **Arsenic (As) :** It is the most poisonous element of V<sup>th</sup> group.

**ABNORMAL BEHAVIOUR OF NITROGEN**

- (a) Nitrogen is a gas, while other elements are solids.  
 (b) Nitrogen molecule is diatomic ( $N_2$ ) while molecules of P, As and Sb are tetra atomic ( $P_4, As_4, Sb_4$ ) and that of Bi is mono atomic.  
 (c) Halides of nitrogen except  $NF_3$  are highly explosive.  
 (d)  $N_2O_3$  and  $N_2O_5$  are monomeric while trioxides and pentoxides of P, As and Sb are dimeric.  
 (e) It is chemically inert due to the presence of triple bond other elements are highly reactive due to presence of single bond in their molecule.  
 (f)  $N \equiv N, C = O, (C \equiv N)^-$  are isoelectronic species but  $N \equiv N$  is less reactive due to nonpolar nature and high ionisation energy.  
 (g) N does not form sulphides.  
 (h) Nitrogen occurs in free state but others are not.

**COMPOUNDS OF V-A GROUP****(I) FORMATION OF HYDRIDES**

- (a) Hydrides formed have  $YH_3$  formula -  $\{NH_3, PH_3, AsH_3, SbH_3, BiH_3\}$   
 (b) Except  $NH_3$ , all Hydrides are poisonous.  
 (c)  $NH_3$  neutralises protic acids as well as aprotic acids (Lewis Acid) so ammonia is strong base.  
 (d)  $PH_3 + HI \longrightarrow PH_4I$   
       Phosphene                      Phosphonium Iodide.  
       Phosphene is a weak base as compared to  $NH_3$  and rest all have amphoteric nature.  
 (e)  $NH_3$  will have high boiling point due to H-bond.  
 (f) Tendency of H-bonding and B.P.  
        $NH_3 > PH_3 < AsH_3 < SbH_3 < BiH_3$ .  
 (g)  $NH_3$  cannot acts as a reducing agent and  $BiH_3$  is strongest reducing agent.  
 (h) Stability decreases from  $NH_3$  to  $BiH_3$   
        $\therefore$  Size increases and so bond strength decreases.  
 (i) Oxidation state :  
       Hydrazine         $NH_2 - NH_2$  or  $N_2H_4 \Rightarrow -2$   
       Hydrazoic Acid  $N_3H \Rightarrow -1/3$   
        $NH_2 - OH \Rightarrow -1$



- (j) Hydrazine is used as propellant for rocket fuels  
 $\therefore$  It undergoes combustion releasing large amount of energy.
- (k)  $\text{H}_2\text{O}_2$  also a better propellant than  $\text{N}_2\text{H}_4$   
 $\therefore$   $\text{H}_2\text{O}_2$  provides nascent O which is more reactive than  $\text{O}_2$ .
- (l)  $\text{N}_3^-$  is called Azide Ion  $\longrightarrow$  Has 4 lone pair  
 Eg.  $\text{Ba}^{+2}\text{N}_3^- \longrightarrow$  Barium Azide  $[\text{Ba}(\text{N}_3)_2]$ .

## (II) FORMATION OF HALIDES

(i)  $\text{YX}_3$  (ii)  $\text{YX}_5$

- (i) **Tri Halides** : All possible trihalides of all these elements are known except  $\text{NCl}_3$ ,  $\text{NBr}_3$ , and  $\text{NI}_3$   
 Because:

- (1) Low polarity of the N – X bond.
- (2) Weakness of N – X bond due to large size difference.
- (3)  $\text{NCl}_3 + 3\text{H}_2\text{O} \longrightarrow \text{NH}_3 + 3\text{HOCl}$   
 $\text{PCl}_3 + 3\text{H}_2\text{O} \longrightarrow \text{H}_3\text{PO}_3 + 3\text{HCl}$   
 $\text{SbCl}_3 + 3\text{H}_2\text{O} \longrightarrow \text{SbOCl} + 2\text{HCl}$  (Stibynl Chloride)  
 $\text{BiCl}_3 + \text{H}_2\text{O} \longrightarrow \text{BiOCl} + 2\text{HCl}$  (Bismithyl Chloride)

When an aq. solution of  $\text{BiCl}_3$  is prepared, after some time a turbidity appears which is milky in appearance and finally a white ppt is formed due to formation of  $\text{BiOCl}$ .

- (4) Lewis Base Order :  
 $\text{NF}_3 < \text{NCl}_3 < \text{NBr}_3 < \text{NI}_3$ .

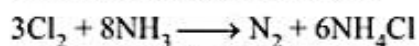
## (ii) Penta Halides :

- (1) Except N and Bi all forms pentahalides, N does not form due to absence of d-orbital Bi does not form due to inert pair effect.
- (2)  $\text{PCl}_5$  acts as an effective chlorinating Agent so it decomposes into  $\text{PCl}_5 \longrightarrow \text{PCl}_3 + \text{Cl}_2$

## (III) NITROGEN ( $\text{N}_2$ )

**Preparation of  $\text{N}_2$  :**

- $\text{NH}_4\text{NO}_2 \xrightarrow{\Delta} \text{N}_2 + 2\text{H}_2\text{O}$
- $(\text{NH}_4)_2\text{Cr}_2\text{O}_7 \xrightarrow{\Delta} \text{N}_2 + 4\text{H}_2\text{O} + \text{Cr}_2\text{O}_3$
- $\text{Ba}(\text{N}_3)_2 \xrightarrow{\Delta} \text{Ba} + 3\text{N}_2$  } Purest  $\text{N}_2$  obtained  
 $2\text{NaN}_3 \xrightarrow{\Delta} 2\text{Na} + 3\text{N}_2$  } by this method
- $2\text{NH}_3 + 3\text{NaOCl} \longrightarrow \text{N}_2 + 3\text{NaCl} + 3\text{H}_2\text{O}$
- $2\text{NO} + 2\text{Cu} \longrightarrow 2\text{CuO} + \text{N}_2$   
 (red, overheated) (Black)
- $\text{Cl}_2$  passed into liquor  $\text{NH}_3$   
 $3\text{Cl}_2 + 2\text{NH}_3 \longrightarrow \text{N}_2 + 6\text{HCl}$   
 $6\text{NH}_3 + 6\text{HCl} \longrightarrow 6\text{NH}_4\text{Cl}$



In this method  $\text{NH}_3$  conc. should not be lowered down beyond a particular limit.



(Trimendously explosive)



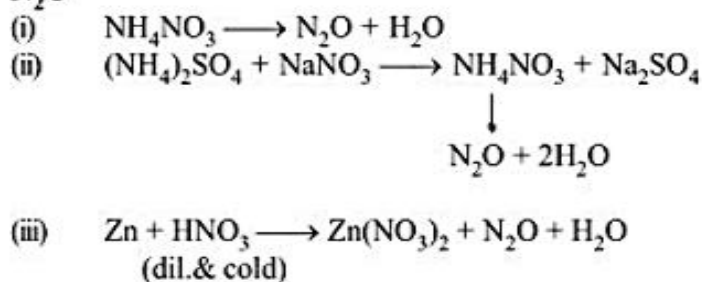


## (IV) OXIDES OF NITROGEN

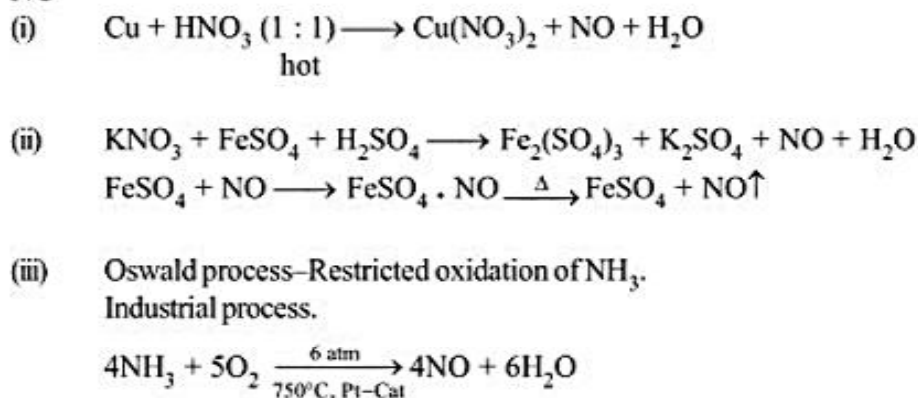
Oxides of nitrogen	Structure	Physical state	Colour of gas
N <sub>2</sub> O	$\bar{N} \equiv \overset{+}{N} = O$	Gas	Colourless
NO	$:\dot{N}=\ddot{O}: \text{ or } :N \equiv O:$	Gas	Colourless
N <sub>2</sub> O <sub>3</sub>	$\begin{array}{c} O \\ \parallel \\ N - N = O \\ \diagup \quad \diagdown \\ O \quad \quad O \end{array} ; O = N - O - \overset{\parallel}{N} O$		Blue liquid (–30°C)
NO <sub>2</sub>	$2N \begin{array}{c} O \\ \parallel \\ \diagdown \\ O \end{array} \rightleftharpoons \begin{array}{c} O \\ \parallel \\ O - N - N = O \\ \diagup \quad \diagdown \\ O \quad \quad O \end{array}$	Gas	Brown
N <sub>2</sub> O <sub>5</sub>	$\begin{array}{c} O \\ \parallel \\ N - O - N = O \\ \diagup \quad \diagdown \\ O \quad \quad O \end{array}$	Colourless solid	–(no existence in gas phase)

### Preparations:

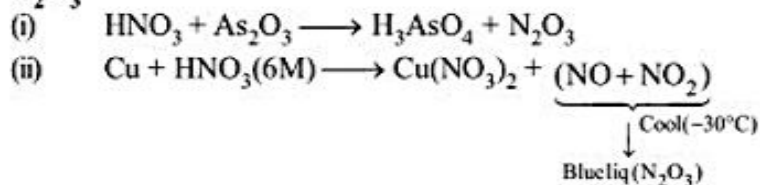
#### 1. N<sub>2</sub>O

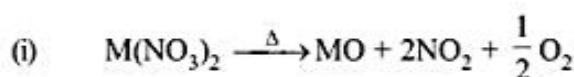


#### 2. NO

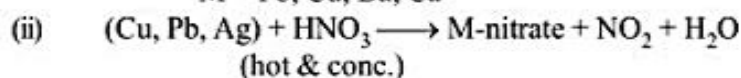


#### 3. N<sub>2</sub>O<sub>3</sub>

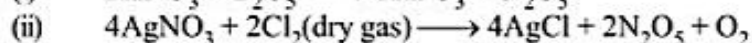
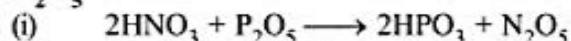




$M = Pb, Cu, Ba, Ca$

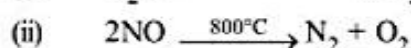
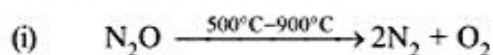


## 5. $N_2O_5$

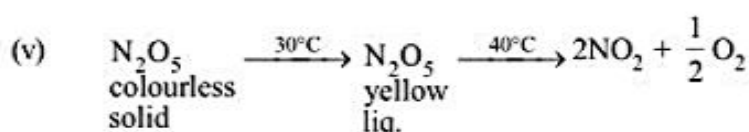
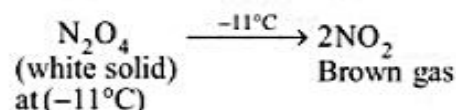
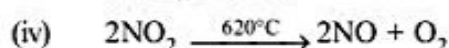


**Properties:**

### (I) Decomposition Behaviour



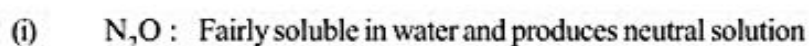
(Blue liq.) at  $(-30^\circ C)$



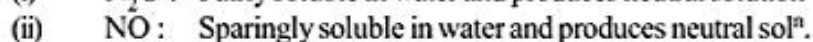
### (II) Reaction with $H_2O$ & $NaOH$

$H_2O$

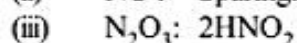
$NaOH$



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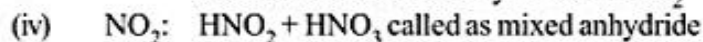


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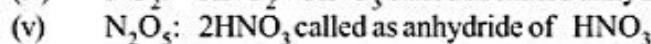


Hence it is known as anhydride of  $HNO_2$

$NaNO_2$

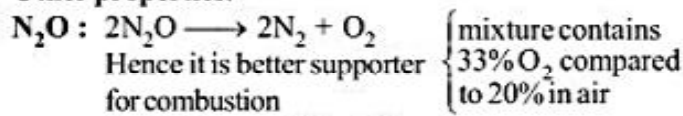


$NaNO_2 + NaNO_3$

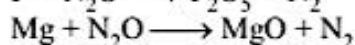
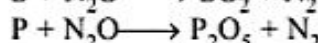
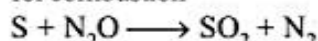


$NaNO_3$

**Other properties:**



{ mixture contains  
33%  $O_2$  compared  
to 20% in air



- NO :**
- (i) It burns :  $\text{NO} + \frac{1}{2} \text{O}_2 \longrightarrow \text{NO}_2$
  - (ii) It supports combustion also for molten sulphur and hot phosphorous.  
 $\text{S} + 2\text{NO} \longrightarrow \text{SO}_2 + \text{N}_2$   
 $2\text{P} + 5\text{NO} \longrightarrow \text{P}_2\text{O}_5 + \frac{5}{2} \text{N}_2$
  - (iii) It is being absorbed by  $\text{FeSO}_4$  solution.
  - (iv) It is having reducing property.  
 $\text{KMnO}_4 + \text{NO} + \text{H}_2\text{SO}_4 \longrightarrow \text{K}_2\text{SO}_4 + \text{MnSO}_4 + \text{HNO}_3 + \text{H}_2\text{O}$   
 $\text{HOCl} + \text{NO} + \text{H}_2\text{O} \longrightarrow \text{HNO}_3 + \text{HCl}$
  - (v) NO shows oxidising property also.  
 $\text{SO}_2 + 2\text{NO} + \text{H}_2\text{O} \longrightarrow \text{H}_2\text{SO}_4 + \text{N}_2\text{O}$   
 $\text{H}_2\text{S} + 2\text{NO} \longrightarrow \text{H}_2\text{O} + \text{S} \downarrow + \text{N}_2\text{O}$   
 $3\text{SnCl}_2 + 2\text{NO} + 6\text{HCl} \longrightarrow 3\text{SnCl}_4 + 2\text{NH}_2\text{OH}$   
 (Used for  $\text{NH}_2\text{OH}$  preparation)
  - (vi) NO combines with  $\text{X}_2$  ( $\text{X}_2 = \text{Cl}_2, \text{Br}_2, \text{F}_2$ ) to produce  $\text{NOX}$   
 $2\text{NO} + \text{X}_2 \longrightarrow 2\text{NOX}$

**$\text{N}_2\text{O}_3$  :** No more properties.

**$\text{NO}_2$  : (1)** It is having oxidising property.  
 $\text{S} + \text{NO}_2 \longrightarrow \text{SO}_2 + \text{NO}$   
 $\text{P} + \text{NO}_2 \longrightarrow \text{P}_2\text{O}_5 + \text{NO}$   
 $\text{C} + \text{NO}_2 \longrightarrow \text{CO}_2 + \text{NO}$   
 $\text{SO}_2 + \text{NO}_2 + \text{H}_2\text{O} \longrightarrow \text{H}_2\text{SO}_4 + \text{NO}$   
 $\text{H}_2\text{S} + \text{NO}_2 \longrightarrow \text{H}_2\text{O} + \text{S} \downarrow + \text{NO}$   
 $\text{CO} + \text{NO}_2 \longrightarrow \text{CO}_2 + \text{NO}$

**NO not formed :**  $2\text{KI} + 2\text{NO}_2 \longrightarrow \text{I}_2 + 2\text{KNO}_2$

- (2) Reducing property of  $\text{NO}_2$ .  
 $\text{KMnO}_4 + \text{NO}_2 + \text{H}_2\text{SO}_4 \longrightarrow \text{K}_2\text{SO}_4 + \text{MnSO}_4 + \text{HNO}_3 + \text{H}_2\text{O}$   
 $\text{O}_3 + 2\text{NO}_2 \longrightarrow \text{O}_2 + \text{N}_2\text{O}_5$   
*not the reduction product of  $\text{O}_3$*

**$\text{N}_2\text{O}_5$  :**  $\text{I}_2 + 5\text{N}_2\text{O}_5 \longrightarrow \text{I}_2\text{O}_5 + 10\text{NO}_2$   
 $\text{I}_2\text{O}_5$  is used for the estimation of CO  
 $\text{I}_2\text{O}_5 + 5\text{CO} \longrightarrow \text{I}_2 + 5\text{CO}_2$   
 $\text{I}_2 + 2\text{S}_2\text{O}_3^{2-} \longrightarrow 2\text{I}^- + \text{S}_4\text{O}_6^{2-}$   
 $\text{N}_2\text{O}_5 + \text{NaCl} \longrightarrow \text{NaNO}_3 + \text{NO}_2\text{Cl}$

This likes proves that  $\text{N}_2\text{O}_5$  is consisting of ion pair of  $\text{NO}_2^+$  &  $\text{NO}_3^-$



### Oxy acids of Nitrogen

S.No.	Name of acids	Formula	Oxidation No. of N
1.	Hyponitrous acid	$\text{H}_2\text{N}_2\text{O}_2$ or $\text{HNO}$	+1
2.	Hydroxynitrous acid or Nitroxyl acid	$\text{H}_4\text{N}_2\text{O}_4$ or $\text{H}_2\text{NO}_2$	+2
3.	Nitrous acid	$\text{HONO}$ or $\text{HNO}_2$	+3
4.	Pernitrous acid	$\text{HOONO}$	+4
5.	Nitric acid	$\text{HNO}_3$	+5
6.	Pernitric acid	$\text{HNO}_4$	+6

### (V) NITRIC ACID ( $\text{HNO}_3$ )

It was named aqua fortis (means strong water) by alchemists.

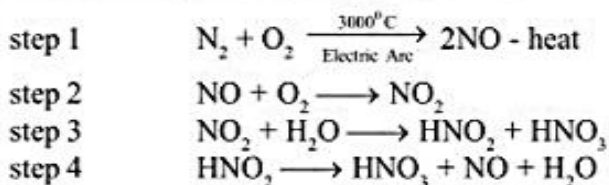
#### Preparation

##### (i) Laboratory Method

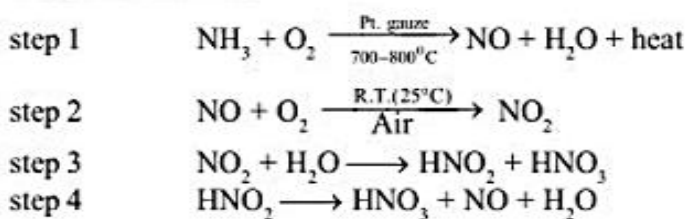
$\text{KNO}_3 + \text{conc. H}_2\text{SO}_4 \longrightarrow \text{KHSO}_4 + \text{HNO}_3(\text{vap})$   
vapours of nitric acid evolved are condensed in a glass receiver.

##### (ii) Industrial Preparation

##### (A) Birkeland Eyde Process or arc process



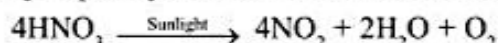
##### (B) Ostwald's Process



#### Properties

##### Physical

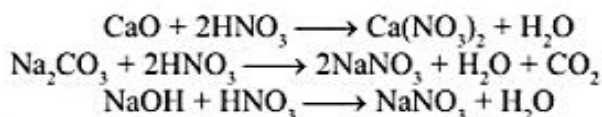
Nitric acid usually acquires yellow colour due to its decomposition by sunlight into  $\text{NO}_2$ .



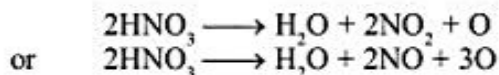
The yellow colour of the acid can be removed by warming it to  $60-80^\circ\text{C}$  and bubbling dry air through it. It has extremely corrosive action on the skin and causes painful sores.

##### Chemical

- (a) It is very strong acid. It exhibits usual properties of acids. It reacts with basic oxides, carbonates, bicarbonates and hydroxides forming corresponding salts.

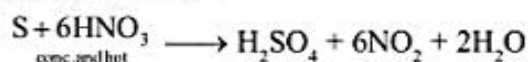


- (b) **Oxidising nature:** Nitric acid acts as a strong oxidising agent as it decomposes to give nascent oxygen easily.

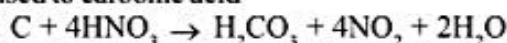


- (i) **Oxidation of non-metals:** The nascent oxygen oxidises various non-metals to their corresponding highest oxyacids.

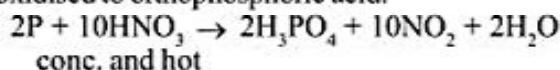
- (1) Sulphur is oxidised to sulphuric acid



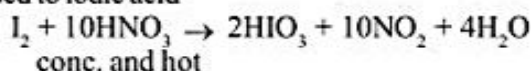
- (2) Carbon is oxidised to carbonic acid



- (3) Phosphorus is oxidised to orthophosphoric acid.

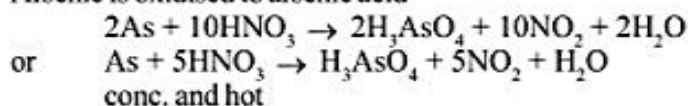


- (4) Iodine is oxidised to iodic acid

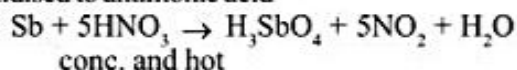


- (ii) **Oxidation of metalloids :** Metalloids like non-metals also form highest oxyacids

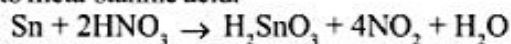
- (1) Arsenic is oxidised to arsenic acid



- (2) Antimony is oxidised to antimonic acid

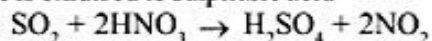


- (3) Tin is oxidised to meta-stannic acid.

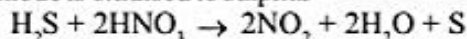


- (iii) **Oxidation of Compounds:**

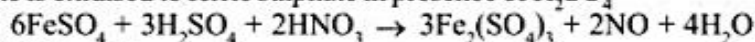
- (1) Sulphur dioxide is oxidised to sulphuric acid



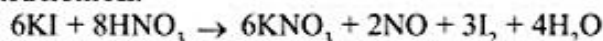
- (2) Hydrogen sulphide is oxidised to sulphur



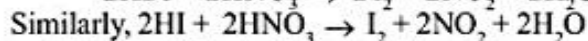
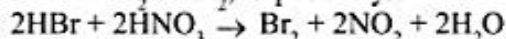
- (3) Ferrous sulphate is oxidised to ferric sulphate in presence of  $\text{H}_2\text{SO}_4$



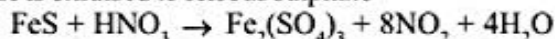
- (4) Iodine is liberated from KI.



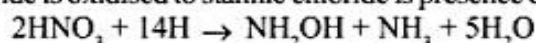
- (5) HBr, HI are oxidised to  $\text{Br}_2$  and  $\text{I}_2$ , respectively.



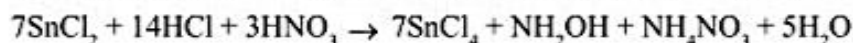
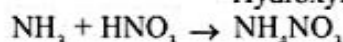
- (6) Ferrous sulphide is oxidised to ferrous sulphate



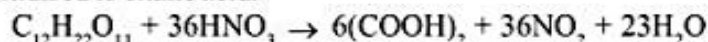
- (7) Stannous chloride is oxidised to stannic chloride in presence of HCl.



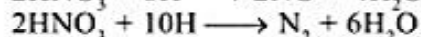
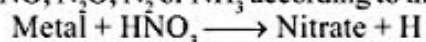
Hydroxylamine



- (8) Cane sugar is oxidised to oxalic acid.



- (c) **Action on Metals:** Most of the metals with the exception of noble metals like gold and platinum are attacked by Nitric acid. Nitric acid plays a double role in the action of metals, i.e., it acts as an acid as well as an oxidising agent. Armstrong postulated that the primary action of nitric acid is to produce hydrogen in the nascent form. Before this hydrogen is allowed to escape, it reduces the nitric acid into a number of products like  $\text{NO}_2$ ,  $\text{NO}$ ,  $\text{N}_2\text{O}$ ,  $\text{N}_2$  or  $\text{NH}_3$  according to the following reactions:



The progress of the reaction is controlled by a number of factors:

- the nature of the metal,
- the concentration of the acid,
- the temperature of the reaction,
- the presence of other impurities.

Concentration of nitric acid	Metal	Main Products
Very dilute $\text{HNO}_3$ (6%)	Mg, Mn	$\text{H}_2$ + Metal nitrate
	Fe, Zn, Sn	$\text{NH}_4\text{NO}_3$ + metal nitrate + $\text{H}_2\text{O}$
Dilute $\text{HNO}_3$ (20%)	Pb, Cu, Ag, Hg	$\text{NO}$ + metal nitrate + $\text{H}_2\text{O}$
	Fe, Zn	$\text{N}_2\text{O}$ + metal nitrate + $\text{H}_2\text{O}$
	Sn	$\text{NH}_4\text{NO}_3$ + $\text{Sn}(\text{NO}_3)_2$
Conc. $\text{HNO}_3$ (70%)	Zn, Fe, Pb, Cu, Ag	$\text{NO}_2$ + metal nitrate + $\text{H}_2\text{O}$
	Sn	$\text{NO}_2$ + $\text{H}_2\text{SnO}_3$ Metastannic acid

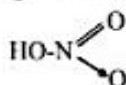
#### Action on Proteins

- Nitric acid attacks proteins forming a yellow nitro compound called xanthoprotein. It, therefore, stains skin and renders wool yellow. This property is utilized for the test of proteins.
- Oxidation** A number of organic compounds are oxidised. Sawdust catches fire when nitric acid is poured on it. Turpentine oil bursts into flames when treated with fuming nitric acid. Cane sugar is oxidised to oxalic acid. Toluene is oxidised to benzoic acid with dil.  $\text{HNO}_3$ .

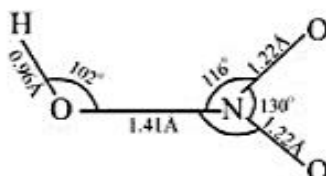


**Structure**

Nitric acid is a monobasic acid, i.e., the molecule consists of one hydroxyl group as it is formed by the hydrolysis of nitryl chloride,  $\text{NO}_2\text{Cl}$ . It may be structurally represented as below:



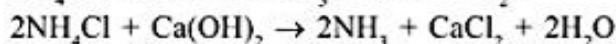
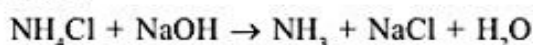
Gaseous nitric acid is a planar molecule. The bond lengths and bond angles as present in the molecule are represented in the figure:

**(VI) AMMONIA ( $\text{NH}_3$ )**

**Discovery :** - Berthelot, in 1788, pointed out that ammonia is a compound of nitrogen and hydrogen. In 1800, Davy established its formula  $\text{NH}_3$ .

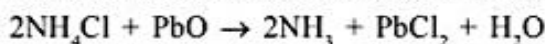
**\* Preparation :**

- (i) Ammonia is obtained on a small scale from ammonium salts which evolve it when heated with caustic soda or lime.

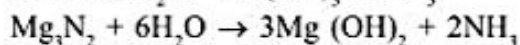
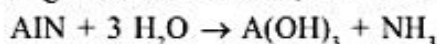


(Slaked lime)

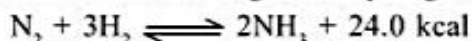
- (ii) Ammonia is formed when ammonium chloride is heated with litharge



- (iii) By reacting nitrides with water, ammonia is obtained.

**MANUFACTURE OF AMMONIA**

- (i) **Haber's process : Principle :** Haber process is the most important industrial method of preparing ammonia. This method was discovered by a German chemist Fritz Haber. The method involves the direct combination of nitrogen and hydrogen according to the following reaction.



The reaction is reversible, exothermic and formation of  $\text{NH}_3$  is followed by a decrease in volume. According to Le Chatelier's principle, the optimum conditions for the greater yield of ammonia are:

- (a) **High pressure :** Usually a pressure of 200 atmospheres is applied.
- (b) **Low temperature :** The working temperature of  $450-550^\circ\text{C}$  is maintained.



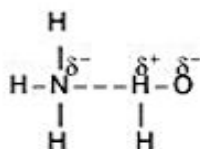
- (c) **Catalyst :** At low temperature, although the yield of ammonia is more yet the reaction is very slow. In order to speed up the reaction, a catalyst is used. The following catalysts have been proposed for this purpose.

- (i) Finely divided iron with some molybdenum as a promotor.
- (ii) Finely divided nickel and sodalime deposited over pumice stone.

**Raw materials :** Nitrogen and hydrogen are the chief raw materials. Nitrogen is obtained from air by liquefaction followed by fractional evaporation of liquid air. Hydrogen is obtained by electrolysis of water.

**Physical properties :**

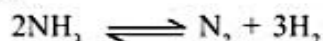
- (i) Ammonia is a colourless gas with a characteristic pungent odour. It brings tears into the eyes.
- (ii) It is lighter than air .
- (iii) It is highly soluble in water. One volume of water dissolves 1300 volume of ammonia at 0°C and 1 atmosphere. The high solubility is due to the hydrogen bonding. The solubility of ammonia increase with increase of pressure and decreases with increase of temperature.



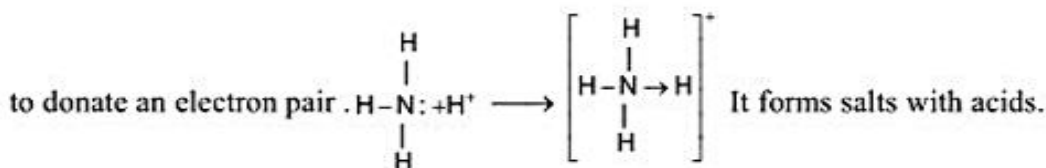
- (iv) It can be easily liquefied at room temperature by the application of pressure. The liquid ammonia is colorless and boils at -33°C. It freezes at -78°C. Liquid ammonia has a large heat of vaporization (327 cal/g.). It is, therefore, used in ice-plants.

**\* Chemical Properties :**

- (i) **Stability :** It is highly stable. It decomposes into nitrogen and hydrogen at red heat or when electric sparks are passed throughout it .

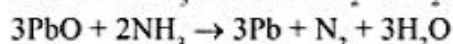
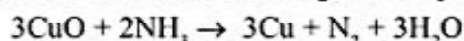


- (ii) **Basic nature :** Ammonia is a Lewis base, accepting proton to form ammonium ion as it has tendency

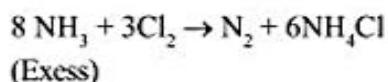
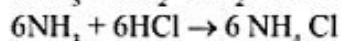
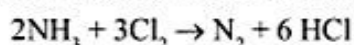


Thick white fumes

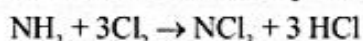
- (iii) **Oxidation :** It is oxidised to nitrogen when passed over heated CuO or PbO.



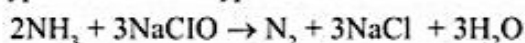
Both chlorine and bromine oxidise ammonia.



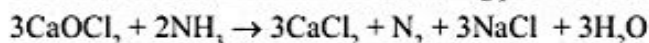
When chlorine is in excess an explosive substance nitrogen trichloride is formed.



Hypochlorites and hypobromite oxidise ammonia to nitrogen.



The oxidation of ammonia with bleaching powder occurs on warming.



Thus, ammonia acts as a reducing agent.

#### Uses :

- (i) Liquid ammonia is used in refrigeration on account of its large heat of evaporation.
- (ii) Ammonia is used in the form of ammonium hydroxide (aq. solution) in the laboratory in qualitative and quantitative analysis.
- (iii) Ammonia is used for making artificial silk.
- (iv) It is used as a cleansing agent for removing grease.

#### \* Phosphorous :

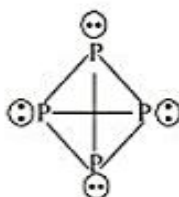
- (1) Phosphorous is largely used in match industry.
- (2) White phosphorous is used as a rat poison.

### PHOSPHOROUS

#### TYPES OF PHOSPHOROUS

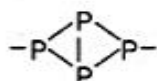
- (i) Yellow or white Phosphorous
- (ii) Red Phosphorous
- (iii) Black Phosphorous

#### (i) White P :



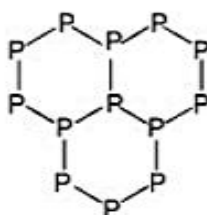
- (a) White P exist as discrete  $\text{P}_4$  molecules. It has tetrahedral geometry. Bond angle is  $60^\circ$  instead of  $109^\circ$ . With this Bond angle white P is associated with strain and because it is less stable or more reactive.
- (b) Ignition temp of white P is  $30^\circ\text{C}$ . i.e. it is highly reactive and when it undergoes ignition, it releases large amount of energy and this energy is emitted in form of light which is called as Fluorescence. i.e. white P glows into dark.
- (c) Because of high reactivity of white P it is stored on  $\text{H}_2\text{O}$ .
- (d) White P slowly changes into Red P and it will get yellow colouration and finally Red.
- (e) If Red P has little % of white P in it as impurity then it is purified by adding NaOH white P undergoes reaction whereas red P not.
- (f) White P is highly poisonous.

## (ii) Red P :



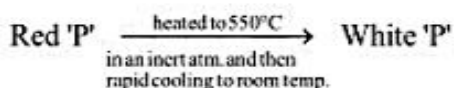
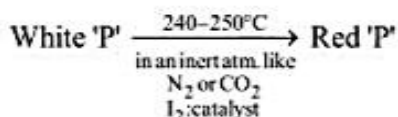
- (a) Formed from white P by breakage of one P – P bond and so chain of  $P_4$  molecules is formed.
- (b) Long chain of  $P_4$  molecules are formed and when compared with white P, red P has more density, less reactive with Breakage of P – P bond, strain related with  $P_4$  molecules decreases.
- (c) Ignition temp of red P is above  $230^\circ\text{C}$

## (iii) Black P :

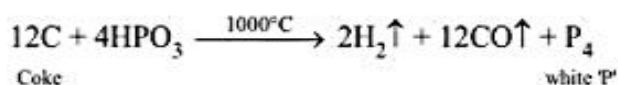
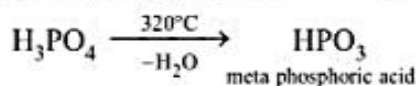
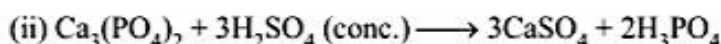
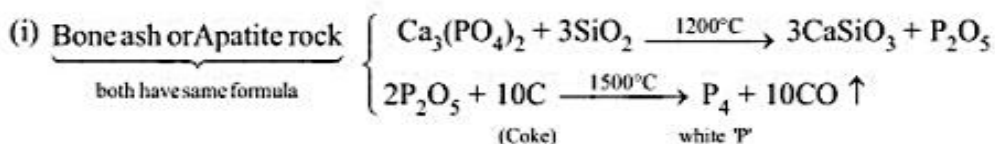


- (a) Exist in the form of Hexagonal layers like graphite.
- (b) It is least reactive and has maximum density.
- (c) Black P exist as solid of high density.
- (d) It is a conductor of electricity.

## INTERCONVERSION OF WHITE 'P' &amp; RED 'P'



## Preparation of white 'P'



## REACTIONS OF 'P'

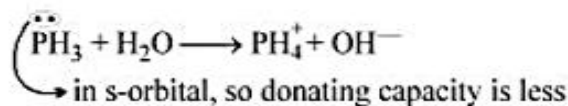
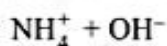
- \*  $P + H_2SO_4 \text{ (hot \& conc.)} \longrightarrow H_3PO_4 + SO_2 + H_2O$
- \*  $P + KIO_3 + H_2SO_4 \longrightarrow H_3PO_4 + I_2 + K_2SO_4$
- \* Reaction with hot metal —
  - $3Na + P \longrightarrow Na_3P$
  - $3Mg + 2P \longrightarrow Mg_3P_2$
  - $3Ca + 2P \longrightarrow Ca_3P_2$
  - $2Cu + 2P \longrightarrow Cu_3P_2$
  - $Al + P \longrightarrow AlP$
  - $Ca_3P_2 + H_2O \longrightarrow M(OH)_n + PH_3$
  - or  $Mg_3P_2$  or  $AlP$

## PREPARATION OF $PH_3$ (PHOSPHINE GAS)

- (i)  $4H_3PO_3 \xrightarrow{\Delta} PH_3 + 3H_3PO_4$
  - (ii)  $PH_4I + KOH \longrightarrow KI + PH_3 + H_2O$   
( $PH_3 + HI$ )
  - (iii)  $2AlP + 3H_2SO_4 \longrightarrow Al_2(SO_4)_3 + PH_3 \uparrow$
- } Purest  $PH_3$

## Physical Properties

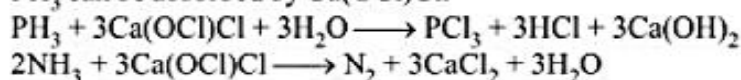
- (i) It is having 'rotten fish' smell
- (ii) It is soluble in  $CS_2$  and insoluble in water.  
( $NH_3$  is soluble in water)



$PH_4^+$  is formed with acids

- (iii) Like  $NH_3$ ,  $PH_3$  also can form addition product.

$CaCl_2 \cdot 8NH_3$ ,  $Cu_2Cl_2 \cdot 2PH_3$ ,  $AlCl_3 \cdot 2PH_3$ ,  $SnCl_4 \cdot 2PH_3$   
 $PH_3$  can be absorbed by  $Ca(OCl)Cl$ .



## OTHER REACTIONS OF $PH_3$

- (i)  $PH_3 + O_2 \xrightarrow{150^\circ} P_2O_5 + H_2O$
- (ii)  $PH_3 + 3Cl_2 \longrightarrow PCl_3 + 3HCl$
- (iii)  $PH_3 + 4N_2O \xrightarrow[\text{sparking}]{\text{electrical}} H_3PO_4 + 4N_2$





**The Elements are** O, S, Se, Te, Po  
(Chalcogens)

$$\text{H}_2\text{S}_4 \quad \text{H}-\text{S}-\text{S}-\text{S}-\text{S}-\text{H}$$

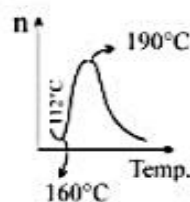
## SULPHUR CHEMISTRY

- \* **Allotropes:**
- |                                      |  |            |
|--------------------------------------|--|------------|
| (i) Rhombic or $\alpha$ -sulphur.    | $\left. \begin{array}{l} S(\alpha) \xrightleftharpoons[95.5^\circ\text{C}]{95.5^\circ\text{C}} S(\beta) \\ \text{below} \qquad \qquad \text{above} \end{array} \right\}$ | $S(\beta)$ |
| (ii) Monoclinic or $\beta$ -sulphur. |  |            |
| (iii) $\gamma$ -Sulphur              |  |            |

**Amorphous forms are**

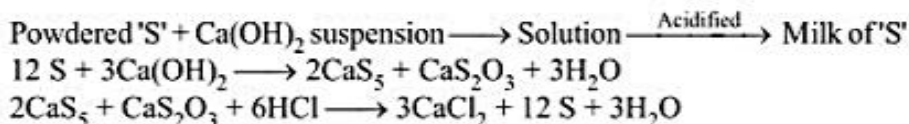
- (i) Plastic sulphur
- (ii) Milk of sulphur
- (iii) Colloidal sulphur

- \* Viscosity of 'S' with temperature:  
m.p. of 'S'  $\longrightarrow$  112.8°C.



- (i)  $> 112.8^\circ\text{C}$  to  $160^\circ\text{C} \Rightarrow$  slow decreases due to  $S_8$  rings slip and roll over one another easily.
- (ii)  $> 160^\circ\text{C}$ , increases sharply due to breaking of  $S_8$  rings into chains and polymerases into large size chain.
- (iii)  $190^\circ\text{C}$ , again large chains are being broken into small chain.

- \* **Milk of sulphur :**



- \* **Colloidal Sulphur :**
- $$\text{Na}_2\text{S}_2\text{O}_3 + 2\text{HCl} \longrightarrow 2\text{NaCl} + \text{H}_2\text{O} + \text{SO}_2 + \text{S} \downarrow$$
- $$2\text{H}_2\text{S} + \text{SO}_2 \longrightarrow 3\downarrow + 2\text{H}_2\text{O}$$

- Props. of 'S' :**
- (a) Thin Cu-strip catches fire in sulphur vapour.  
 $\text{Cu} + \text{S} \longrightarrow \text{CuS}$ .
  - (b) 'S' burns spontaneously in fluorine.  $\text{S} + 3\text{F}_2 \longrightarrow \text{SF}_6$   
 $\text{Cl}_2$  passed into liq. sulphur  $\Rightarrow 2\text{S} + \text{Cl}_2 \rightarrow \text{S}_2\text{Cl}_2$
  - (c)  $\text{S} + 2\text{H}_2\text{SO}_4 \longrightarrow 3\text{SO}_2 + 2\text{H}_2\text{O}$   
 $\text{S} + 2\text{HNO}_3 \longrightarrow \text{H}_2\text{SO}_4 + 2\text{NO}$
  - (d)  $4\text{S} + 6\text{KOH} \longrightarrow 2\text{K}_2\text{S} + \text{K}_2\text{S}_2\text{O}_3 + 3\text{H}_2\text{O}$
  - (e) Burns in air :  $\text{S} + \text{O}_2 \longrightarrow \text{SO}_2$

## FAMILY MEMBERS OF VI<sup>TH</sup> GROUP

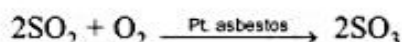
- \* **Oxygen : (O)**

- (i) **Oxygen Molecule ( $\text{O}_2$ ) :**

- (1) In air as  $\text{O}_2$  to the extent of 21% by volume or 23% by weight.
- (2) Lab method to produce  $\text{O}_2$  is.  
 $2\text{NaO}_2 + 2\text{H}_2\text{O} \longrightarrow 4\text{NaOH} + \text{O}_2$
- (3) Air is liquefied by use of joule - Thomson effect {cooling by expansion of gas}.

**(4) Reaction with compounds :**

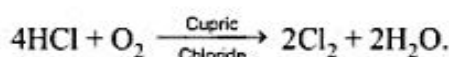
(a) Contact Process :



(b) Ostwald Process :



(c) Deacon's Process :

**(5) Uses :**

- (a) Oxy-Acetylene flame is used for cutting process and welding process.  
 (b) Liquid oxygen is a constituents of fuels used in rockets.

\*

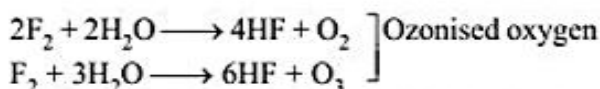
**Oxides :**

A binary compound of oxygen with another element is called an oxide.

- (a) Oxygen combined nearly with all other elements except inert gases, noble metals and halogens.  
 (b) The binary compounds of oxygen with other element are called oxides. Hence, the compounds of oxygen and fluorine ( $\text{OF}_2$ ,  $\text{O}_2$ ,  $\text{F}_2$ ) are not called as oxides.

**OZONE**

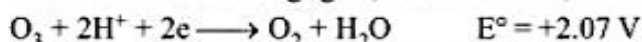
Unstable deep blue, diamagnetic gas, with fishy smell. Toxic enough (more toxic than KCN). It's intense blue colour is due to the absorption of red light.



These are separated by passing into spiral tube cooled into liquid air. Ozone condenses at  $-112.4^\circ\text{C}$ .  
 [b.p. of  $\text{O}_2$   $-183^\circ\text{C}$  ; b.p. of liq. air is  $-190^\circ\text{C}$ ]

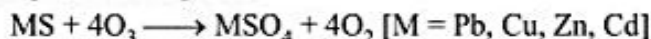
***Oxidising property of  $\text{O}_3$*** 

It is one of best oxidising agent, in acid solution, its standard, reduction potential value is 2.07 V.



It is next to  $\text{F}_2$ . [above 2.07 V, only  $\text{F}_2$ ,  $\text{F}_2\text{O}$  are there]

(i) Metal Sulphides to Sulphates.

(ii)  $2\text{HX} + \text{O}_3 \longrightarrow \text{X}_2 + \text{H}_2\text{O} + \text{O}_2$  [X = Cl, Br, I](iii) Moist S, P, As +  $\text{O}_3 \Rightarrow$ 

(vi)  $\text{alk.} \left\{ \begin{array}{l} \text{KI} + 3\text{O}_3 \longrightarrow \text{KIO}_3 + 3\text{O}_2 \\ \text{KI} + 4\text{O}_3 \longrightarrow \text{KIO}_4 + 4\text{O}_2 \end{array} \right\}$



- (v) Hg loses its fluidity (tailing of Hg)  

$$2\text{Hg} + \text{O}_3 \longrightarrow \text{Hg}_2\text{O} + \text{O}_2$$
 similarly  $2\text{Ag} + \text{O}_3 \longrightarrow \text{Ag}_2\text{O} + \text{O}_2$

Brown

- (vi)  $\text{BaO}_2 + \text{O}_3 \rightarrow \text{BaO} + 2\text{O}_2$   
 $\text{H}_2\text{O}_2 + \text{O}_3 \longrightarrow \text{H}_2\text{O} + 2\text{O}_2$   
 $\text{Na}_2\text{O}_2 + \text{O}_3 + \text{H}_2\text{O} \longrightarrow 2\text{NaOH} + 2\text{O}_2$

**Absorbent:** (i) Turpentine oil

(ii) Oil of cinnamon

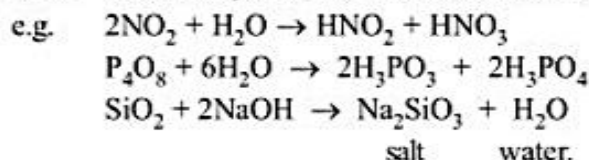
**Uses:** (i) Sterilising water

(ii) Detection of position of the double bond in the unsaturated compound.

### Classification of oxides

- (1) **Acidic oxides**  $\rightarrow \text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{H}_2\text{CO}_3$ .  
 e.g.  $\text{CO}_2$ ,  $\text{B}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{N}_2\text{O}_3$ ,  $\text{NO}_2$ ,  $\text{N}_2\text{O}_5$ ,  $\text{P}_4\text{O}_6$

**Note:** Mixed anhydrides  $\rightarrow$  Those oxides which form two oxy acids.



- (2) **Basic oxides :**

Oxide +  $\text{H}_2\text{O} \rightarrow$  alkali ; e.g.  $\text{Na}_2\text{O} + \text{H}_2\text{O} \rightarrow 2\text{NaOH}$

Oxide + acid  $\rightarrow$  salt +  $\text{H}_2\text{O}$  ; e.g.  $\text{CuO} + \text{H}_2\text{SO}_4 \rightarrow \text{CuSO}_4 + \text{H}_2\text{O}$

Oxide + Acidic oxide  $\rightarrow$  salt ; e.g.  $\text{PbO} + \text{SO}_3 \rightarrow \text{PbSO}_4$ .

- (3) **Neutral Oxide:**

Oxide + Acid  $\rightarrow$  No reaction

Oxide + Base  $\rightarrow$  No reaction

e.g.  $\text{CO}$ ,  $\text{H}_2\text{O}$ ,  $\text{N}_2\text{O}$ ,  $\text{NO}$  etc.

- (4) **Amphoteric oxides**  $\rightarrow$  React with acid & base both to form salts.

e.g.  $\text{ZnO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{BeO}$ ,  $\text{Sb}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{PbO}$ ,  $\text{PbO}_2$  etc.

$\text{ZnO} + 2\text{NaOH} \rightarrow \text{Na}_2\text{ZnO}_2 + \text{H}_2\text{O}$  ;  $\text{ZnO} + 2\text{HCl} \rightarrow \text{ZnCl}_2 + \text{H}_2\text{O}$

$\text{Al}_2\text{O}_3 + 2\text{NaOH} \rightarrow 2\text{NaAlO}_2 + \text{H}_2\text{O}$  ;  $\text{Al}_2\text{O}_3 + 6\text{HCl} \rightarrow 2\text{AlCl}_3 + 3\text{H}_2\text{O}$

$\text{PbO} + 2\text{NaOH} \rightarrow \text{Na}_2\text{PbO}_2 + \text{H}_2\text{O}$  ;  $\text{PbO} + \text{H}_2\text{SO}_4 \rightarrow \text{PbSO}_4 + \text{H}_2\text{O}$

$\text{Cr}_2\text{O}_3 + 2\text{NaOH} \rightarrow \text{Na}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{O}$  ;  $\text{Cr}_2\text{O}_3 + 3\text{H}_2\text{SO}_4 \rightarrow \text{Cr}_2(\text{SO}_4)_3 + 3\text{H}_2\text{O}$

- (5) **Compound or mixed oxides**  $\rightarrow$  Oxides which behaves as mixture of two simple oxides.

e.g.  $\text{Pb}_3\text{O}_4$  ( $2\text{PbO} + \text{PbO}_2$ )

$\text{Fe}_3\text{O}_4$  ( $\text{FeO} + \text{Fe}_2\text{O}_3$ )

$\text{Mn}_3\text{O}_4$  ( $2\text{MnO} + \text{MnO}_2$ )

- (6) **Peroxides**  $\rightarrow$  Oxides + dil acids  $\rightarrow$   $\text{H}_2\text{O}_2$   
 e.g.  $\text{Na}_2\text{O}_2 + \text{H}_2\text{SO}_4(\text{dil}) \rightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}_2$   
 $\text{BaO}_2 + \text{H}_2\text{SO}_4(\text{dil}) \rightarrow \text{BaSO}_4 + \text{H}_2\text{O}_2$
- (7) **Dioxides**  $\rightarrow$  Like peroxides, these also contain excess of oxygen but do not form  $\text{H}_2\text{O}_2$  with dilute acids. They evolve chlorine with conc.  $\text{HCl}$  and oxygen with conc.  $\text{H}_2\text{SO}_4$ .  
 e.g.  $\rightarrow \text{PbO}_2, \text{MnO}_2$   
 $\text{MnO}_2 + 4\text{HCl conc.} \rightarrow \text{MnCl}_2 + \text{Cl}_2 + 2\text{H}_2\text{O}$   
 $2\text{MnO}_2 + 2\text{H}_2\text{SO}_4(\text{conc.}) \rightarrow 2\text{MnSO}_4 + \text{O}_2 + 2\text{H}_2\text{O}$
- (8) **Suboxides**  $\rightarrow$  The oxides which contain less oxygen than expected from the normal valency of the elements are termed sub-oxides.  
 e.g. Carbon suboxide -  $\text{C}_3\text{O}_2$   
 Lead suboxide -  $\text{Pb}_3\text{O}$   
 Nitrous oxides -  $\text{N}_2\text{O}$
- (9) **Superoxides**  $\rightarrow$  These oxides contain  $\text{O}_2^-$  ion.  
 e.g.  $\text{KO}_2, \text{RbO}_2, \text{CsO}_2$ .  
 These react with water to give hydrogen peroxide and oxygen.  
 $2\text{KO}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{KOH} + \text{H}_2\text{O}_2 + \text{O}_2$

- \* **Sulphur (S):**  
**Atomic Number : 16**  
 Outer electronic configuration :  $3s^2 3p_x^2 3p_y^1 3p_z^1$   
 Number of unpaired electrons : 2  
 Covalency : 2  
 Oxidation States : -2, 0, +2, +4, +6

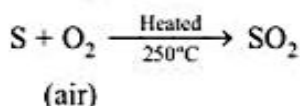
**Occurrence :** Sulphur is one of the widely occurring element. It constitutes about 0.1 percent of the earth's crust. It is found in free (native) as well as combined state. In the combined state it occurs as sulphides and sulphates.

1. **As sulphides :** Cinnabar ( $\text{HgS}$ ), Galena ( $\text{PbS}$ ), Zinc blende ( $\text{ZnS}$ ), Copper pyrites ( $\text{CuFeS}_2$ )
2. **As Sulphates :** Gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), barytes ( $\text{BaSO}_4$ ), epsomite ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ). Organic substances such as eggs, proteins onions, garlic, mustard, hair and wool contain sulphur.

### Properties

#### \* Physical Properties :

1. Sulphur is a pale yellow, crystalline, brittle solid. It is odourless and tasteless.
2. It has no physiological action on human beings as it is poisonous to lower organisms.
3. It is poor conductor of heat and a bad conductor of electricity. Hence sulphur is a very good insulator.
4. It is insoluble in water but soluble in carbon disulphide, sparingly soluble in alcohol and ether.
5. **Burning :** When heated to about  $250^\circ\text{C}$  sulphur burns in air with a pale blue flame forming mainly

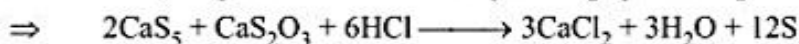


**USES :**

1. For vulcanization of rubber.
2. In match industry and fireworks.
3. As a disinfectant for houses, for destroying bacteria, fungi, insects, etc.
4. For the manufacture of  $\text{SO}_2$ ,  $\text{CS}_2$ ,  $\text{H}_2\text{SO}_4$  etc.
5. In manufacture of sulphur dyes.
6. In skin medicines.
7. For preparing gun powder (a mixture of charcoal, sulphur and potassium nitrate).
8. Po is radioactive element

\* **Allotropic forms of Sulphur :****(i) Rhombic octahedral or  $\alpha$ -sulphur :****(ii) Monoclinic Prismatic or  $\beta$ -sulphur :**

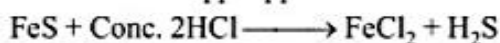
- (a) These two sulphur are called as enantiatropic substances  
 $\alpha$  - sulphur  $\rightleftharpoons$   $\beta$  - sulphur.
- (b)  $\alpha$  and  $\beta$  sulphur are crystalline and rest being amorphous and exist as  $\text{S}_8$  cyclic molecule.

**(iii) Plastic or  $\gamma$  sulphur :** It is obtained by quenching of boiling sulphur in a thin stream to cold water.**(iv) Milk of sulphur :** It is obtained by boiling milk of lime with sulphur and decomposing the products with HCl.

Milk of sulphur is soluble in  $\text{CS}_2$  and is mainly used in medicine

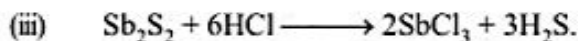
**(v) Colloidal or  $\delta$ -sulphur :** It is prepared by passing  $\text{H}_2\text{S}$  through a solution of an oxidising agent\* **Uses of Sulphur :**

- (a) In manufacture of  $\text{H}_2\text{SO}_4$ ,  $\text{CS}_2$  gun powder etc.
- (b) Vulcanisation of rubber.

**COMPOUNDS OF SULPHUR****Hydrogen sulphide ( $\text{H}_2\text{S}$ ) :****(i)** Also known as sulphurated hydrogen.**(ii)** Lab method : Kipps apparatus

In this reaction conc.  $\text{HNO}_3$  cannot be employed because  $\text{HNO}_3$  is a oxidising agent and converts  $\text{H}_2\text{S}$  into colloidal sulphur.





Antimony sulphide

Here  $\text{H}_2\text{S}$  is rotten egg smelling gas. If conc.  $\text{HNO}_3$  or  $\text{H}_2\text{SO}_4$  is added the rotten smell of  $\text{H}_2\text{S}$  disappears.

(iv) **Properties :**

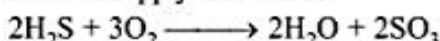


This would be confirmatory test for  $\text{H}_2\text{S}$ .

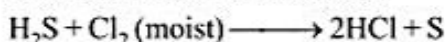
(2) It burns in air with a blue flame.



If the air supply is in excess.



(3) It reduces moist chlorine to  $\text{HCl}$



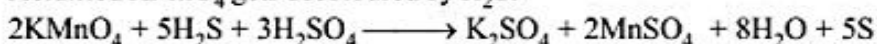
(4) It is a mild acid



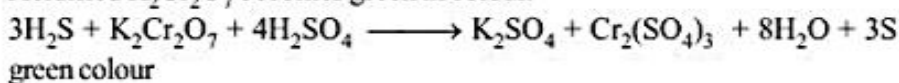
(5) Ferric salts reduced to ferrous salts



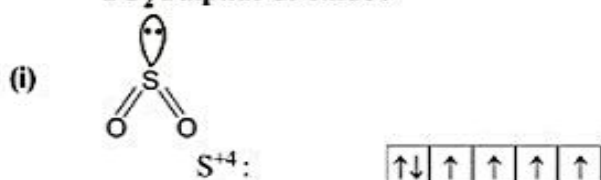
(6) Acidified  $\text{KMnO}_4$  gets decoloured by  $\text{H}_2\text{S}$ .



(7) Acidified  $\text{K}_2\text{Cr}_2\text{O}_7$  becomes green in colour.



\*  **$\text{SO}_2$  Sulphur di-oxide :**

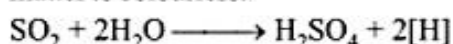


\*  $\pi$  bond for nuclei  $d\pi - p\pi$  bond.

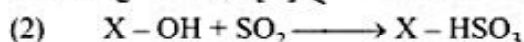
\* v - shape or trigonal planar.

(ii) **Bleaching Property :**  $\text{SO}_2$  acts as a bleaching agent in following two ways.

(1) In the presence of  $\text{H}_2\text{O}$ , it is oxidised with the liberation of nascent hydrogen which reduces the colouring matter to colourless.



Colouring matter +  $2[\text{H}] \rightleftharpoons$  Colourless compound.

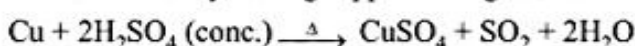


Coloured

Colourless

(iii) **Preparations :**

(1) **Lab Method :** By heating copper turnings with conc.  $\text{H}_2\text{SO}_4$ .

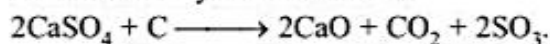


(2) By roasting  $\text{ZnS}$  or iron pyrites.





(3) Reaction of anhydride with coke :

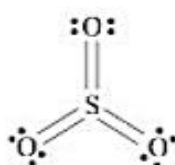


(iv) **Physical Properties :**

(1) It is pungent smelling suffocating gas

(2) It is soluble in  $\text{H}_2\text{O}$

\* **Sulphur trioxide ( $\text{SO}_3$ ) :**



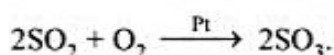
triagonal planar molecule.

(1) **Preparation :**

1. Action of heat on Ferric sulphate



2. **Commercial Method :** By the oxidation of dry  $\text{SO}_2$  with dry oxygen.



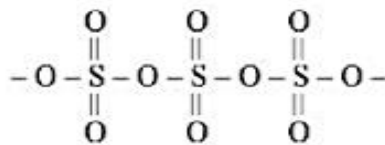
$\text{SO}_2$  and  $\text{O}_2$  are first dried by passing through conc.  $\text{H}_2\text{SO}_4$  and then passed over heated ( $400^\circ\text{C}$ ) platinised asbestos contained in a hard glass tube.

(2) **Physical Properties :** It exists in atleast three forms  $\alpha\text{-SO}_3$ ,  $\beta\text{-SO}_3$  and  $\gamma\text{-SO}_3$

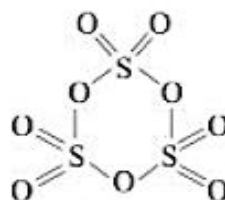
The structure of solid  $\text{SO}_3$  is complex. It possesses cyclic trimer ( $\alpha$  form) structure.

(a)  **$\alpha$  form:** It is branched and sheet like structure

(b)  **$\beta$  and  $\gamma$  forms :** It possesses an infinite helical chain made up of linked  $\text{SO}_4$  tetrahedron.



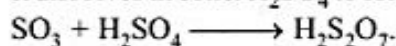
$\beta$  - form



$\gamma$  - form

(3) **Chemical Reactions :**

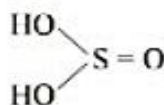
1. It dissolves in conc.  $\text{H}_2\text{SO}_4$  to form pyrosulphuric acid (oleum)



2.  $\text{SO}_3 + 2\text{HBr} \longrightarrow \text{H}_2\text{O} + \text{Br}_2 + \text{SO}_2$ . In this  $\text{SO}_3$  is used as an oxidising agent.

\* **Oxy Acids of Sulphur :**

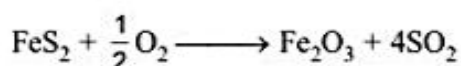
(a) **Sulphurous Acid ( $\text{H}_2\text{SO}_3$ ) :**



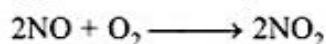
Structure of Sulphurous Acid ( $\text{H}_2\text{SO}_3$ )

(b) **Sulphuric Acid ( $\text{H}_2\text{SO}_4$ ) or oil of vitrol :**

Preparation : Mainly two process used

**(A) Lead Chamber Process :****Note :**

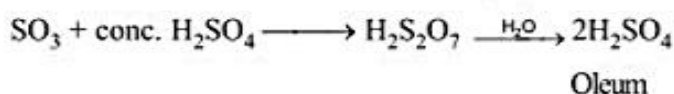
1. NO (Nitric Oxide) produced takes oxygen from air and gets converted back to nitrogen dioxide. Thus oxide of nitrogen take oxygen from air and pass it to  $SO_2$  and thus act as oxygen carriers.



2. It is seen that in the presence of an insufficient quantity of steam or water spray, lead chamber crystals of the composition  $SHSO_4$ . No are obtained.

**(B) Contact Process :**

Initially Pt. was employed as catalyst but now  $V_2O_5$  is used because Pt is poisonous.

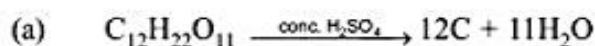


- (1) To get the appropriate amount of  $H_2SO_4$  contact process is utilised.
- (2) If bottle of  $H_2SO_4$  is opened, it absorbs unlimited amount of moisture and  $H_2SO_4$  overflows to conc.  $H_2SO_4$  is deliquescent liquid which is highly viscous and has high density.
- (3) When  $H_2SO_4$  is done dilute by adding water the reaction being highly exothermic so temperature increases to  $120^\circ C$  and thus along with water vapour the energy released when conc.  $H_2SO_4$  is contacted with skin, causing burning.
- (4)  $\text{Conc. } H_2SO_4 + \text{Glucose} \longrightarrow 6C + 6H_2O$

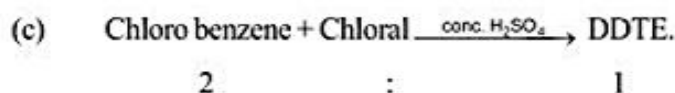
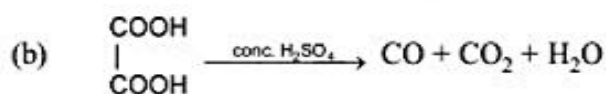
The white sugar changes to black and this is called charring of sugar (Blackening of sugar). This is the conformation test of  $H_2SO_4$ .

**\* Chemical Reaction of  $H_2SO_4$  :**

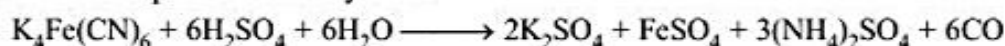
- (1) It has greater affinity for water. Hence is used for drying of all gases except ammonia. It is also employed as dehydrating agent.



This called as charring of sugars.



(2) Action with potassium ferrocyanide:

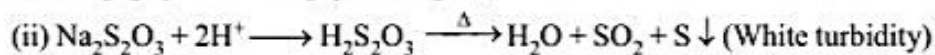
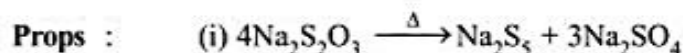
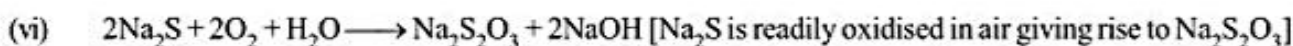
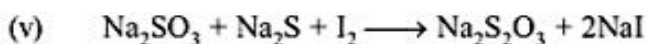
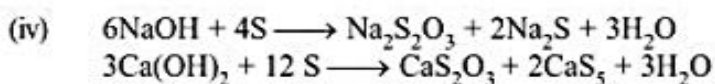
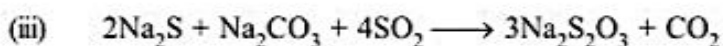
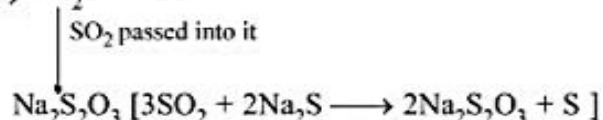
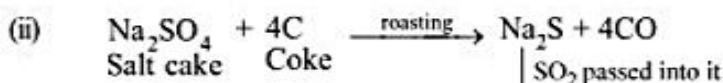
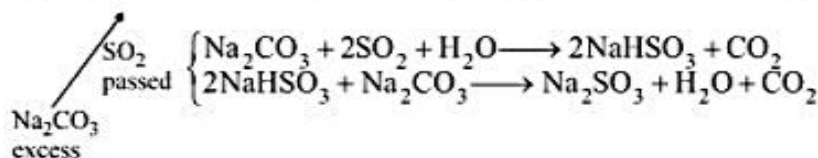
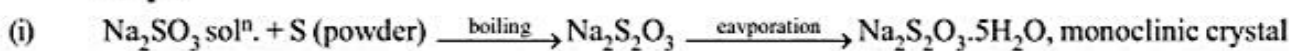


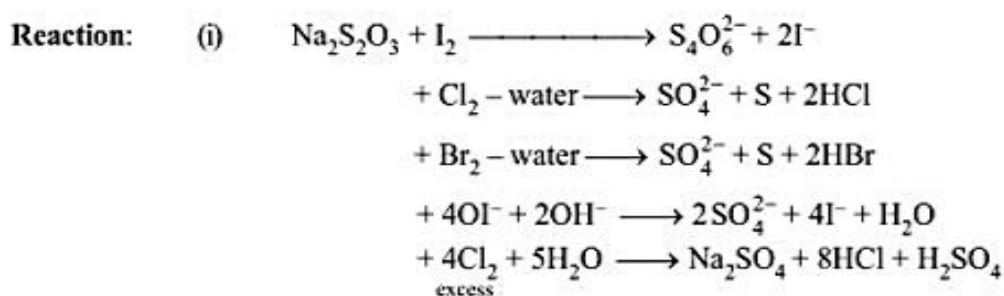
Uses :

- (a) It is regarded as king of chemical.
- (b) In manufacture of explosives (T.N.T, gun cotton) etc.
- (c) As a pickling agent : Pickly is an industrial process for removing layers of basic oxides from metals like Fe and Cu. Before electroplating, galvanizing and soldering.

### SODIUM THIOSULPHATE

Prep<sup>n</sup> :





### Illustration

**Q.1** Compounds A and B are treated with dilute HCl separately. The gases liberated are Y and Z respectively. Y turns acidified  $\text{K}_2\text{Cr}_2\text{O}_7$  paper green while Z turns lead acetate paper black. The compounds A and B are respectively -

(A)  $\text{Na}_2\text{S}$  and  $\text{Na}_2\text{SO}_3$

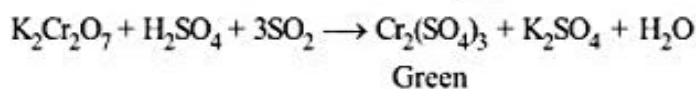
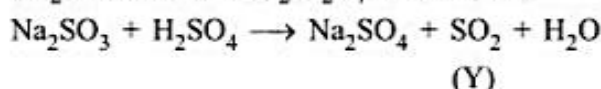
(B)  $\text{Na}_2\text{SO}_3$  and  $\text{Na}_2\text{S}$

(C)  $\text{NaCl}$  and  $\text{Na}_2\text{CO}_3$

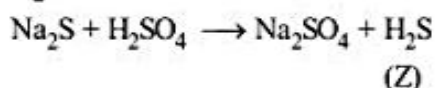
(D)  $\text{Na}_2\text{SO}_3$  and  $\text{Na}_2\text{SO}_4$

**Ans.** (B)

**Sol.**  $\text{SO}_2$  turns acidified  $\text{K}_2\text{Cr}_2\text{O}_7$  paper green.



$\text{H}_2\text{S}$  turns lead acetate paper black.



### Exercise

**Q.1** The correct order of decreasing stability of hexafluorides of group 16 members is -

(A)  $\text{SF}_6 > \text{SeF}_6 > \text{TeF}_6$

(B)  $\text{TeF}_6 > \text{SeF}_6 > \text{SF}_6$

(C)  $\text{SF}_6 > \text{TeF}_6 > \text{SeF}_6$

(D)  $\text{TeF}_6 > \text{SF}_6 > \text{SeF}_6$

**Ans.** (A)





(c) For Cl. Ground State :

Valency = 1



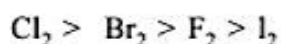
1<sup>st</sup> excited state



\* **Bond Energy :**

F – F bond dissociation energy is less than that of Cl – Cl and Br – Br. It is due to larger inter electronic (electron - electron) repulsion between the non bonding electrons in the 2p orbitals of fluorine atom. then these in the 3p orbitals of chlorine atoms.

F – F	Cl – Cl	Br – Br	I – I
38 kcal/mol	57 kcal/mol	45.5 kcal/mol	35.6 kcal/mol

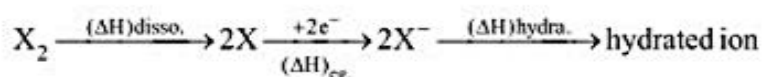


\* **Oxidising Power :**

The electron affinity, or tendency to gain electrons reaches a maximum at chlorine. Oxidation may be regarded as the removal of electron so that an oxidising agent gains electrons.

Thus the halogens act as oxidizing agents.

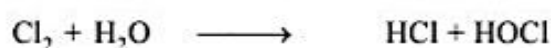
The strength of an oxidising agent (i.e. oxidation potential) depends upon several energy terms and represented by following diagram.



$\Delta H$  (reduction potential) =  $\Delta H$  (dissociation energy) +  $\Delta H$  (electron gain enthalpy) +  $\Delta H$  (hydration energy)

Element	$\Delta H$ (reduction potential)
F <sub>2</sub>	– 186.5
Cl <sub>2</sub>	– 147.4
Br <sub>2</sub>	– 136.4
I <sub>2</sub>	– 122.4

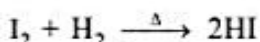
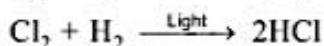
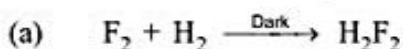
Thus oxidising powers decrease on descending in group VII. Fluorine is so strong oxidising agent that H oxidizes water to oxygen. The oxidation of H<sub>2</sub>O by Cl<sub>2</sub> is thermodynamically possible but since the energy of activation is high this reaction does not occur.



Iodine is even weaker oxidising agent and the free energy change indicate that energy would have to be supplied to make it oxidise water.

## CHEMICAL PROPERTIES

\* **Reaction with  $H_2$  :** All halogens reacts with H to form hydrogen halides.



(b) Reactivity of Halogens  $F > Cl > Br > I$

(c) HCl in gaseous state is hydrogen chloride. While HCl in aqueous solution is hydrochloric acid.

(d) HCl, HBr, HI acts as reducing agent.

(e)  $H_2F_2$  cannot decompose into  $H_2$  and  $F_2$  and so its can never acts as reducing agent.

(f)  $H_2F_2$  has highest boiling point and exist in liquid state.

(g) HCl, HBr and HI exist on gaseous state.

(h) HCl b.p. is very low and after HCl b.p. increases because Vanderwaals forces increases ( $\uparrow$ ) and so b.p. ( $\uparrow$ ).

\* **Reaction With  $H_2O$  :**

(a)  $H_2O$  acts as reducing Agent only with F.



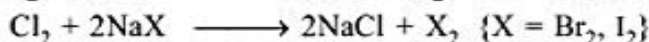
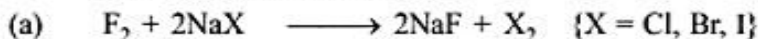
(b)  $Cl_2 + H_2O \longrightarrow HCl + HClO$  Hypochlorous acid  $\xrightarrow{\text{Light}} HCl + [O]$

So  $Cl_2$  in presence of moisture acts as bleaching agent.

(c)  $H_2O + I_2 \longrightarrow$  No Reaction.

(d) All these halogen are soluble in water except  $I_2$  when KI solution is added  $I_2$  will also dissolve because adsorption of  $I_2$  molecule on the surface of iodide ion  $KI_3$  is formed which is a highly ionic compound.

\* **Displacement Reaction :**



So order of displacement  $[F_2 > Cl_2 > Br_2 > I_2]$

(b) If Halogen is in -ve O.S. then it is replaced by more E.N. element.

(c) If Halogen is +ve O.S. then it is replaced by less E.N. element.

\* **Reaction with Metals :** Metal halides are formed  $F > Cl > Br > I$

\* **Reaction with Non Metals :** Non metallic halides are formed. Eg.  $NF_3$ ,  $PCl_3$  etc.



\* **Reaction with  $\text{NH}_3$  :**

- (a)  $3\text{F}_2 + \text{NH}_3 \longrightarrow \text{NF}_3 + 3\text{HF}$   
 (b)  $3\text{Cl}_2 + \text{NH}_3 \longrightarrow \text{NCl}_3 + 3\text{HCl}$   
 (c)  $\text{I}_2$  is less reactive and so remains same and Ammoniated compound will form.  
 $3\text{I}_2 + 2\text{NH}_3 \longrightarrow \text{NI}_3 \cdot \text{NH}_3 + 3\text{HI}$

\* **Reaction with  $\text{NaOH}$  :**

- (a)  $\text{F}_2 + \text{NaOH (dil.)} \longrightarrow 2\text{NaF} + \text{OF}_2 + \text{H}_2\text{O}$   
 (b)  $2\text{F}_2 + 4\text{NaOH (conc.)} \longrightarrow 4\text{NaF} + 2\text{H}_2\text{O} + \text{O}_2$

They are both redox reactions.

- (c)  $\text{Cl}_2 + \text{NaOH} \longrightarrow \text{NaCl} + \text{NaClO}_3 + \text{H}_2\text{O}$   
 (d)  $\text{Br}_2 + \text{NaOH} \longrightarrow \text{NaBr} + \text{NaBrO}_3 + \text{H}_2\text{O}$

\* **Formation of Oxides :**

- (a) No oxides of F because of its maximum E.N. character.  
 (b) Rest forms

$\text{X}_2\text{O}$	$\text{X}_2\text{O}_3$	$\text{X}_2\text{O}_5$	$\text{X}_2\text{O}_7$
+ 1	+ 3	+ 5	+ 7
Eg. $\text{Cl}_2\text{O}$	$\text{Cl}_2\text{O}_3$	$\text{Cl}_2\text{O}_5$	$\text{Cl}_2\text{O}_7$

Molecular formula	Structures
$\text{Cl}_2\text{O}$	
$\text{Cl}_2\text{O}_3$	
$\text{Cl}_2\text{O}_5$	
$\text{Cl}_2\text{O}_7$	

- (c) All these oxides are acidic  
 (d) Acidity decreases down the group and maximum active oxide is  $\text{Cl}_2\text{O}_7$

\* **Formation of Oxyacids :**

- (a) F does not form any oxyacid because High E.N.  
 (b) Rest oxyacids are
- |                                   |                                |                               |                                  |
|-----------------------------------|--------------------------------|-------------------------------|----------------------------------|
| Hypo halous acid ( $\text{HXO}$ ) | Halous acid ( $\text{HXO}_2$ ) | Halic acid ( $\text{HXO}_3$ ) | Perhalic acid ( $\text{HXO}_4$ ) |
| X = +1                            | + 3                            | + 5                           | + 7                              |

- (c) All these oxy acids are acidic  
 (d) Acidity and thermal stability decreases down the group and maximum acidity and thermal stability will be of  $\text{HClO}_4$ .  
 (e) Thermal stability of acids increases with the increasing O.S. of the halogens or with increase in the no. of oxygen atom.



## (f) Oxidising Power :

- (i) All these oxyacids acts as strong oxidizing agents.
- (ii) Stability of anions increases from  $\text{ClO}^-$  to  $\text{ClO}_4^-$ , the oxidising power decreases from  $\text{ClO}^-$  to  $\text{ClO}_4^-$
- (iii) Order of oxidising agent  $\text{HClO} > \text{HClO}_2 > \text{HClO}_3 > \text{HClO}_4$

## \* Miscellaneous Reaction :

- (a)  $\text{I}_2 + \text{Na}_2\text{S}_2\text{O}_3$  (Hypo)  $\longrightarrow$   $2\text{NaI}$  (Colourless) +  $\text{Na}_2\text{S}_4\text{O}_6$   
This reaction is employed for identification of  $\text{I}_2$ .
- (b) Dry  $\text{Cl}_2 + \text{Ca(OH)}_2(\text{s}) \longrightarrow \text{CaOCl}_2$  (Bleaching Powder) +  $\text{H}_2\text{O}$

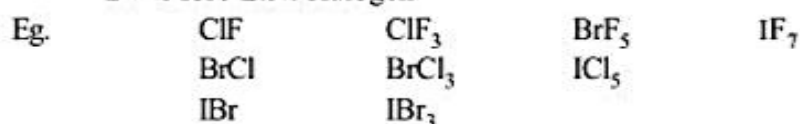
## \* Inter Halogens :

Product obtained by uniting two halogen compounds :



Where A = less E.N. Halogen

B = More E.N. Halogen



These inter halogens have polarity because of different E.N.

**Note : Abnormal Behaviour of Fluorine as Compared to Other Members :**

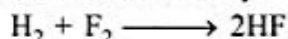
Fluorine differs considerably from other halogens due to -

- (i) Small size
  - (ii) High electronegativity.
  - (iii) Non availability of d - orbitals in its valency shell.
  - (iv) Low bond dissociation energy of F – F bond.
- (a) Boiling point of HF is the highest and for other increases down the group.

**Comparison of  $[\text{Cl}_2, \text{Br}_2$  and  $\text{I}_2]$** 

S.No.	Property	Chlorine	Bromine	Iodine
1.	Physical State	Gas	Liquid	Solid
2.	Colour of Vapour	Greenish Yellow	Dark Red	Violet
3.	Action of $\text{H}_2\text{O}$	Decomposes into $\text{HCl}$ & $\text{O}_2$	Decomposes Slowly in Presence of Light	No action
4.	Oxidising Action	Strong	Good	Weak
5.	Bleaching Action	Moist $\text{Cl}_2$ is a Good Bleaching Agent	Moist $\text{Br}_2$ is a good Bleaching Agent	No Bleaching
6.	Action of Halides	Displaces $\text{Br}_2$ & $\text{I}_2$	Displaces $\text{I}_2$	No Action
7.	Combination with $\text{H}_2$	Explosive in Light Slow in Dark	Only on Heating	Heating + Catalyst

- (b) Due to hydrogen bonding HF is a liquid while HCl, HBr and HI are gases.
- (c) Fluorine, being the most electronegative gives  $\text{SF}_6$  while other member do not form hexahalides with sulphur.
- (d) It exhibits oxidation state of only  $-1$ .
- (e) It is the strongest oxidising agent.
- (f) It liberates oxygen as well as ozone with water.
- (g) HF does not ionize while HCl, HBr and HI ionize in aqueous solution.
- (h) Solubility of salts :
- (i)  $\text{AgF}$  is soluble in water while  $\text{AgCl}$ ,  $\text{AgBr}$  and  $\text{AgI}$  are insoluble.
- (j) It combines with hydrogen with explosion at a low temperature and even in the dark. No other halogens combines so readily.



- (k) It liberates oxygen as well as ozone with water.



## FAMILY MEMBERS OF HALOGEN

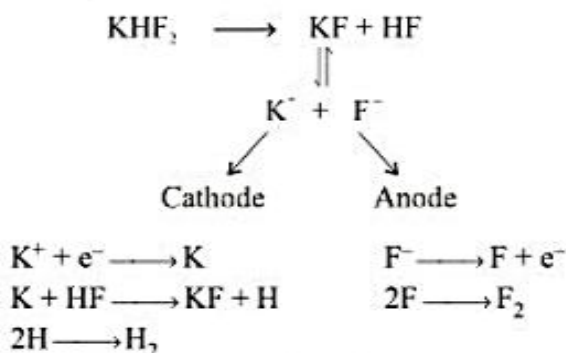
### \* Fluorine ( $\text{F}_2$ ) :

#### Modern method of Isolation :

In this method  $\text{F}_2$  is prepared by the electrolysis of fused fluoride, ( $\text{KHF}_2$ ) potassium hydrogen fluoride.

- \* The electrolytic cells are made of Cu, Ni or monel metal.

Reaction in the electrolytic cell :

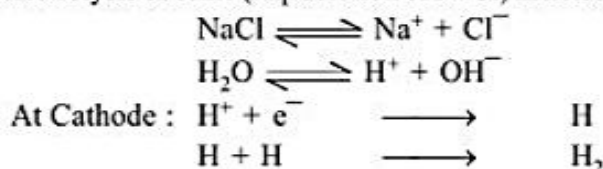


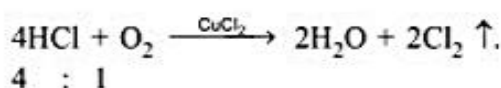
- (i) **Uses :** It is used in the preparation of fluorine compound such as.
- (a) Freon : Freon - 12 i.e.  $\text{CF}_2\text{Cl}_2$  as used in refrigeration and air conditioning in place of  $\text{NH}_3$  and  $\text{SO}_2$ .
- (b) Teflon :  $(-\text{F}_2\text{C} - \text{CF}_2)_n$  It is a new plastic.

### \* Chlorine ( $\text{Cl}_2$ ) :

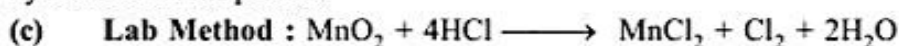
#### (i) Preparation :

- (a) By the electrolysis of brine (Aq. solution of  $\text{NaCl}$ ) in nelson cell. This is the cheapest method



**(b) Decon's Process :**

Chlorine gas thus obtained contains  $\text{N}_2$  and  $\text{O}_2$  and is used for the manufacture of bleaching powder by hansenclaver's process

**(ii) Properties :**

Bleaching:



Coloured matter +  $[\text{O}] \longrightarrow$  Colourless matter.

**(iii) Uses :**

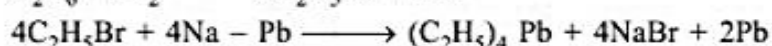
- (a) As a Germicide and disinfectant.
- (b) Domestic antiseptic solution ( $\text{NaOCl}$ )
- (c) In Mfg of bleaching powder, D.D.T etc.
- (d) In warfare gases such as phosgene  $\text{CaOCl}_2$ , tear gas ( $\text{CCl}_3\text{NO}_2$ ) and mustard gas ( $\text{ClC}_2\text{H}_4 - \text{S} - \text{C}_2\text{H}_4\text{Cl}$ )

**\* Bromine ( $\text{Br}_2$ ) :****(i) Preparation :**

**Bittern :** Mother liquor contains about 0.25% of bromine or  $\text{MgBr}_2$  and is known as bittern. Bittern is treated with Chlorine gas.

**(ii) Uses :**

it is used in preparation of ethyl bromide which is used in the mfg of tetraethyl lead (TEL) as an important anti - knock compound in the petroleum industry.

**\* Iodine ( $\text{I}_2$ ) :****(i)  $\text{I}_2$  is the rarest of all the halogens. Its main source is kelp (varee).****(ii) Properties :**

- (a) It is only sparingly soluble in water but readily soluble in Na or K iodide due to formation of triiodide.

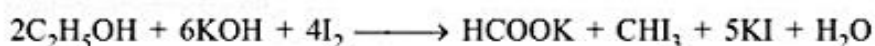


However, this solution behaves as a simple mixture of KI and free  $\text{I}_2$ .

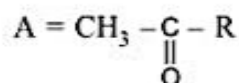
**Note :** Tincture of iodine contains  $\frac{1}{2}$  ounce  $\text{I}_2$ ,  $\frac{1}{4}$  ounce KI and 1 pinch of rectified spirit.



(b) Iodoform Reaction :



Iodoform or Haloform reaction show by following -



When  $\text{R} = \text{H}, \text{CH}_3, \text{C}_2\text{H}_5, \dots$

$\text{R} = \text{Benzyl}$  and its derivatives

$\text{R} = \text{Every 2-Alcohol (not secondary)}$

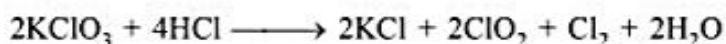
$\text{R} = \text{C}_2\text{H}_5\text{OH}$  (only Ethyl Alcohol in Primary)

$\text{R} = \text{No. tertiary Alcohol.}$

## COMPOUNDS OF DIFFERENT MEMBERS

\* **Potassium Chlorate ( $\text{KClO}_3$ )**

(i) On heating with conc.  $\text{HCl}$ ,  $\text{KClO}_3$  gives a mixture of chlorine and chlorine dioxide known as exchlorine.



(ii) **Uses :** In mfg. of matches, fire works and photographic flash powders.

## PSEUDOHALIDES AND PSEUDOHALOGENS

A few ions are known, consisting of two or more electronegative atoms of which at least one is nitrogen, that have properties similar to those of halide ions. These ions are called pseudohalide ions, Pseudohalide ions are univalent and these form salts resembling halide salts.

The pseudohalide ions are :

Cyanide ions ( $\text{CN}^-$ )	:	Isocyanide ion ( $\text{NC}^-$ )
Cyanate ion ( $\text{OCN}^-$ )	:	Fulminate ion ( $\text{ONC}^-$ )
Thiocyanate ions ( $\text{SCN}^-$ )	:	Isothiocyanate ion ( $\text{NCS}^-$ )
Selenocyanate ion ( $\text{SeCN}^-$ )	:	Tellurocyanate ion ( $\text{TeCN}^-$ )
Azide ion ( $\text{N}_3^-$ )	:	Azido carbon disulphide ion ( $\text{SCSN}_3^-$ )

As the dimers of halide ions are called halogens, the covalent dimers of the pseudohalide ions are called halogens or halogenoids. The pseudohalogens known are :

Cyanogen ( $\text{CN}_2$ )	:	Oxycyanogen ( $\text{OCN}_2$ )
Thiocyanogen ( $\text{SCN}_2$ )	:	Selenocyanogen ( $\text{SeCN}_2$ )
Tellurocyanogen ( $\text{TeCN}_2$ )	:	Azido carbon disulphide ( $\text{SCSN}_3$ )



The best known pseudohalide is  $\text{CN}^-$ . This resembles  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$  in the following respects:

- (i) It forms an acid, HCN.
- (ii) It can be oxidised to  $(\text{CN})_2$  molecule.
- (iii) It forms insoluble salts with  $\text{Ag}^+$ ,  $\text{Pb}^{2+}$  and  $\text{Hg}_2^{2+}$ .
- (iv) It forms large number of complexes similar to halide complexes, e.g.  
 $[\text{Cu}(\text{CN})_4]^{2-}$  and  $[\text{CuCl}_4]^{2-}$ ,  $[\text{Co}(\text{CN})_6]^{3-}$  and  $[\text{CoCl}_6]^{3-}$
- (v) Inter-pseudohalogen compounds  $\text{ClCN}$ ,  $\text{BrCN}$  and  $\text{ICN}$  can be formed.
- (vi)  $\text{AgCN}$  is insoluble in water but soluble in ammonia like  $\text{AgCl}$ .

### Oxy acids of Halogens

Oxidation state of halogens	Chlorine	Bromine	Iodine	Name of acid	Name salt	
+1	$\text{HClO}$	$\text{HBrO}$	$\text{HIO}$	Hypohalous	Hypohalite	Stability and acidity increases but oxidising power decreases
+3	$\text{HClO}_2$	-	-	Halous	Halite	
+5	$\text{HClO}_3$	$\text{HBrO}_3$	$\text{HIO}_3$	Halic	Halate	
+7	$\text{HClO}_4$	$\text{HBrO}_4$	$\text{HIO}_4$	Perhalic	Perhalate	

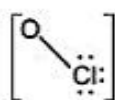
### OXY ACIDS OF HALOGENS

- (1) Fluorine does not form any oxy-acids because it is more electronegative than oxygen.
- (2) Other halogens form four series of oxy acids with formulae  
 $\text{HXO} \rightarrow$  Hypohalous  
 $\text{HXO}_2 \rightarrow$  Halous  
 $\text{HXO}_3 \rightarrow$  Halic  
 $\text{HXO}_4 \rightarrow$  Perhalic acids or Halic (I), Halic (III), Halic (V) and Halic (VII)

#### \* Some important general trends in Oxy-acids of Halogens

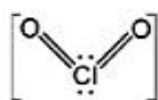
- (1) In oxy-acids, hydrogen is present as  $-\text{OH}$  group
- (2) All the hypohalous acids ( $\text{HXO}$ ) are unstable and readily form  $\text{HXO}_3$ . Among these the relative order of stability is  $\text{HClO} > \text{HBrO} > \text{HIO}$
- (3) In halic acids ( $\text{HXO}_3$ ), iodic acid is the most stable.
- (4) Thermal stability -  
 Thermal stability  $\propto$  oxidation state of halogens & No. of oxygen atoms.  
 (a) The thermal stability of both the acids and their salts increases with the increasing oxidation state of the halogen or with the increase in the number of oxygen atoms i.e. stability of the oxy halide anion increases from  $\text{ClO}^-$ ,  $\text{ClO}_2^-$ ,  $\text{ClO}_3^-$ ,  $\text{ClO}_4^-$ .

- (b) This is due to the fact with the increasing number of oxygen atoms in the series, the no. of electron involved in forming  $\sigma$  and  $\pi$  bonds increases.
- (c) Thus in the most stable perchlorate ion,  $\text{ClO}_4^-$ , all the valence orbitals and electron of chlorine atom are involved in the formation of bonds.
- (d) The stability of perchlorate ion,  $\text{ClO}_4^-$  may also be said due to greater multiplicity of the Cl-O bond.



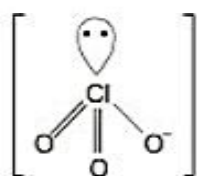
Hypo chlorite

Shape - dumb - bell



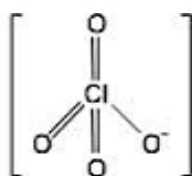
Chlorite

Shape - bent chain



Chlorate

Shape - Pyramidal



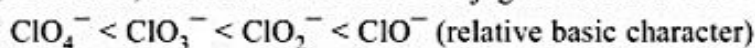
Per- chlorate

Shape - Tetrahedral.

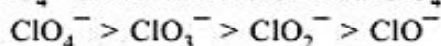
- (5) Oxidising power -  
 $\text{ClO}^-$   
 $\downarrow$  Stability increases and oxidising power decreases  
 $\text{ClO}_4^-$   
 Hypochlorites are the strongest oxidising agents.
- (6) Relative acidity  $\propto$  oxidation no.  
 $\text{HClO}_4 > \text{HClO}_3 > \text{HClO}_2 > \text{HClO}$

**Note :** (i) In all these acids and salts halogen is in  $\text{sp}^3$  hybridised state.

(ii) Stronger the acid, the weaker will be its conjugate base and vice-versa.



Thus  $\text{ClO}_4^-$  is the weakest base and  $\text{HClO}_4$  (conjugate acid of  $\text{ClO}_4^-$ ) is the strongest acid.



Relative stability of Cl-O bonds

**Illustration**

**Q.1** Which of the following is the strongest oxidant –

- (A)  $F_2$  (B)  $Cl_2$  (C)  $Br_2$  (D)  $I_2$

**Ans.** (A)

**Sol.**  $F_2$  is strongest oxidant, because (i)  $F_2$  has exceptionally low dissociation energy of F–F bond, (ii)  $F^-$  has high energy of hydration due to small size of the  $F^-$  ion.

**Exercise**

**Q.1** Solid  $Cl_2O_6$  exists as –

- (A)  $ClO_2^+ ClO_4^-$  (B) Covalent species (C)  $(ClO_3)_2$  (D) None

**Ans.** (A)

**Q.2** Fluorine does not show positive oxidation states because –

- (A) It is most electronegative element  
(B) It forms only anions in ionic compounds  
(C) It cannot form multiple bonds  
(D) It shows non-bonded electron pair repulsion due to small size

**Ans.** (A)

**INERT GAS FAMILY**

Element	Atomic no.	Outer shell configuration
He	2	$1s^2$
Ne	10	$He\ 2s^2 2p^6$
Ar	18	$Ne\ 3s^2 3p^6$
Kr	36	$Ar\ 3d^{10} 4s^2 4p^6$
Xe	54	$Kr\ 4d^{10} 5s^2 5p^6$
Rn	86	$Xe\ 4f^{14} 5d^{10} 6s^2 6p^6$

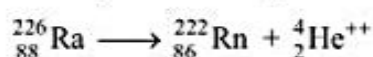
**RARE GASES OR NOBLE GASES**

These are found in atmosphere to very less extent so named rare gases and form very few compounds so termed noble gases.

**Important point**

All have octet configuration except He having duplet configuration.

- (i) They exist on gaseous state.  
(ii) Rn is produced by the disintegration of radium and is radioactive itself



- (iii) Ramsay was the discoverer of these gases.
- (iv) First inert gas which was discovered by Ramsay firstly i.e. argon.
- (v) All except Rn occur in atmosphere almost 1% by volume in which argon is the major constituent.

## ISOLATION

Except He, non-radioactive noble gases are commercially isolated from air by two methods.

- (i) **Fractional Distillation of Liquid air (Claude's Method) :**  
Due to difference in b.p. the various constituents of air are separated from each other.
- (ii) **Dewar's Coconut Charcoal Adsorption Method :**
  - (a)  $O_2$  and  $N_2$  are removed by means of compound formation.
  - (b) The principle of this method is that the adsorption capacity of these gases at low temperature by coconut charcoal increases with increases in their atomic weights.
  - (c) Thus He has the lowest and Xe has the maximum adsorption capacity.

## GENERAL PROPERTIES

- (i) **Atomic Radii, Melting point and Boiling Point, Density :**
  - (a) All increases down the group.
  - (b) He is the only element having two boiling points i.e.  $4.2\text{ K}$  and  $2.5\text{ K}$ .
  - (c) It is [He] only element which exists in two liquid phases i.e. He and  $He_2$ .
  - (d) They are colorless, odourless and tasteless.
- (ii) **Ionisation Energy :**
  - (a) They possess very high ionisation energy.
  - (b) Ionisation energy of Xe is nearly equal to that of molecular oxygen.
- (iii) **Electron Affinity :**  
Due to complete octet, noble gas atoms are unable to take extra electron.
- (iv) **Monatomicity :**  
Due to very high I.E. and nearly zero E.A. noble gas atoms are not capable of combining and their value of  $\gamma = \frac{C_p}{C_v}$  is close to 1.66.
- (v) **Force of attraction between atoms of Noble Gases :**  
Vander Waals force between the atoms increases from He to Xe.
- (vi) **Solubility in Water :**  
Slightly soluble in water and solubility in water increases with increase in atomic number.
- (vii) **Chemical Nature :**
  - (a) Noble gases are almost chemically inert.
  - (b) But Kr, Xe and Rn are slightly reactive because of relatively low IP of gases.



**(viii) Adsorption of Inert Gases :**

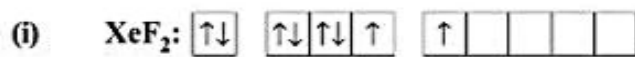
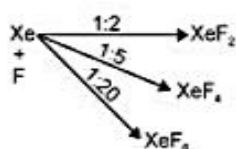
- (a) Done on coconut. Gas particles are adsorbed in surface of coconut charcoal
- (b) Larger the size, more will be the adsorption so maximum adsorption of Xe at highest temp.

**(ix) (a) First gas discovered was Argon. (Ar gas Lazy)**

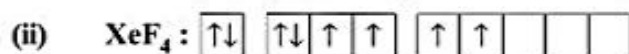
- (b) Other inert gas isolated was Neon.
- (c) Other inert gas remaining hidden gas krypton (Kryptos = Hidden)
- (d) Then Xenon (Xenon = stranger)
- (e) Rn emits  $\alpha$ ,  $\beta$ ,  $\gamma$  radiations.
- (f) He has unusual property of diffusion through lab material like Rubber, Glass, Plastic.

**FAMILY MEMBERS OF NOBLE GASES****\* Xenon (Xe) :**

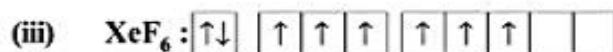
It is the only element that forms true compounds.



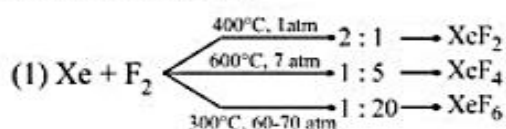
5s      5p      5d  
 $sp^3d$   
 Linear Geometry



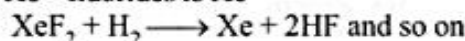
5s      5p      5d  
 $sp^3d^2$   
 Square Planar



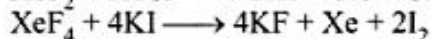
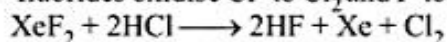
$sp^3d^3$   
 Distorted octahedral

**(iv) Xe – COMPOUNDS****Xenon Fluorides:–**

(2)  $\text{H}_2$  reduces Xe – fluorides to Xe

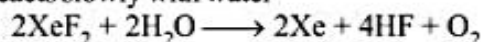


(3) Xe - fluorides oxidise  $\text{Cl}^-$  to  $\text{Cl}_2$  and  $\text{I}^-$  to  $\text{I}_2$

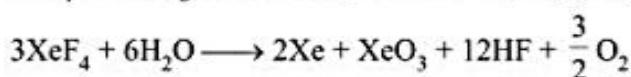


(4) Hydrolysis

$\text{XeF}_2$  reacts slowly with water

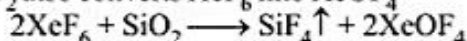


$\text{XeF}_4$  and  $\text{XeF}_6$  react violently with water giving  $\text{XeO}_3$

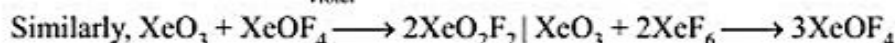


↓  
(explosive, white hygroscopic solid)

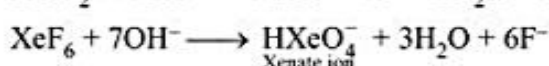
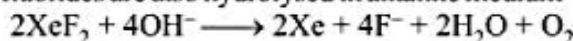
(5)  $\text{SiO}_2$  also converts  $\text{XeF}_6$  into  $\text{XeOF}_4$



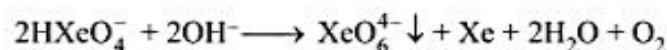
violet



(6) Xe-fluorides are also hydrolysed in alkaline medium

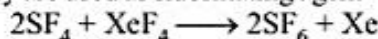


Xenate ion

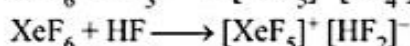
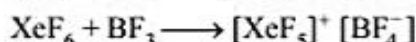
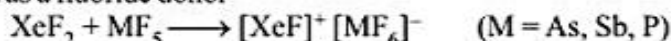


perxenate ion

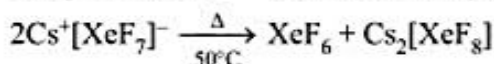
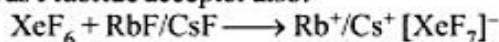
(7) They are used as fluorinating agent



(8) Act as a fluoride donor



(9) Act as Fluoride acceptor also:



(alkali metals fluoride)

#### \* Neon and Argon :

- (i) Gets trapped in the intersitial spaces of  $\text{H}_2\text{O}$  or alcohols and this type of mixture resulted is called as clatharate compound.
- (ii) These compounds are not formed by He.,

**USES**

- (i) Noble gases are widely used to provide inert atmospheres in metallurgical process.
- (ii) He is used as a cooling medium in gas cooled atomic reaction because of its high thermal conductivity, low viscosity and low density.
- (iii) Liquid He is used in gas thermometer required for low temperature measurement.
- (iv) Neon in neon lamps.
- (v) Neon in neon tubes for rectifiers, voltage regulators etc.
- (vi) Argon is in filling in incandescent lamps.
- (vii) Xe is used in discharge tube for quick photography.
- (viii) Rn is used in treatment of cancer (Radiotherapy)

**Illustration**

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- Q.1** Noble gases can be separated by –
- (A) Passing them through some solution
  - (B) Electrolysis of their compounds
  - (C) Adsorption and desorption on coconut charcoal
  - (D) None

**Ans.** (C)

**Sol.** Coconut charcoal possess characteristic property for adsorbing different noble gases at different temperatures.

- Q.2** Which of the following noble gases does not form clathrates?
- (A) He                      (B) Br<sub>2</sub>                      (C) Ar                      (D) Xe

**Ans.** (A)

**Sol.** Due to small size of He it does not form clathrates.

---

**Exercise**

---

- Q.1** The first compound of noble gases prepared by N-Bartlett was –
- (A)  $\text{Xe}^+[\text{Pt F}_6]^-$       (B)  $\text{XeF}_4$                       (C)  $\text{XeF}_6$                       (D)  $\text{XeOF}_4$

**Ans.** (A)

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## SOLVED EXAMPLES

**Q.1** Pick out the incorrect statement.

- (A) central oxygen in  $O_3$  is  $sp^2$  hybridised      (B) the two O—O bonds in  $O_3$  are equal  
(C) with  $BaO_2$ ,  $O_3$  reacts to produce  $H_2O_2$       (D)  $O_3$  causes tailing of mercury

**Ans.** (C)

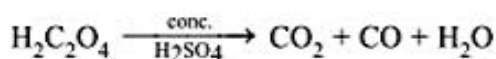
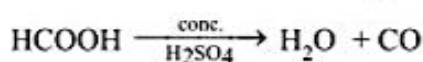
**Sol.** Only (c) is wrong because  $BaO_2 + O_3 \rightarrow BaO + 2O_2$ . The rest of the alternatives are correct.

**Q.2** Carbon monoxide is formed by the action of concentrated  $H_2SO_4$  on

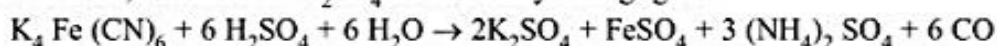
- (A) formic acid      (B) oxalic acid  
(C) potassium ferrocyanide      (D) all of these

**Ans.** (D)

**Sol.** The reaction of concentrated  $H_2SO_4$  on all the compounds is as follows



In these reactions, concentrated  $H_2SO_4$  acts as a dehydrating agent.

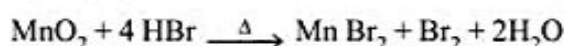
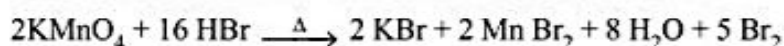


**Q.3** Bromine is formed when concentrated HBr is heated with

- (A)  $KMnO_4$       (B)  $K_2Cr_2O_7$       (C)  $MnO_2$       (D) All of these

**Ans.** (D)

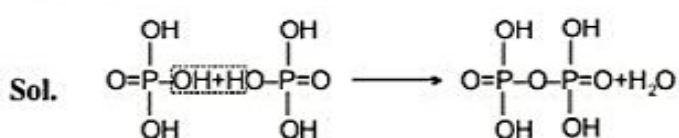
**Sol.** Concentrated HBr reacts with these compounds as follows:



**Q.4** Pick out out incorrect statement -

- (A) Orthophosphorus acid can be obtained by reacting  $P_4O_6$  with  $H_2O$   
(B) Orthophosphoric acid can be obtained by reacting  $P_4O_{10}$  with  $H_2O$   
(C) Pyrophosphoric acid can be obtained by heating orthophosphorous acid  
(D) Metaphosphoric acid is obtained by the dehydration of orthophosphoric acid at  $316^\circ C$ .

**Ans.** (C)



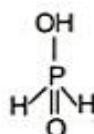
**Q.5** Hypophosphorus acid  $H_3PO_2$  is -

- (A) Tribasic acid      (B) Dibasic acid      (C) Monobasic acid      (D) Not acidic at all

**Ans.** (C)



**Sol.** Structure of Hypophosphorus acid. As it contains only one replaceable H atom. it is mono basic.



**Q.6** Maximum covalency of sulphur is –

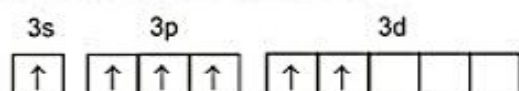
- (A) 2 (B) 4 (C) 6 (D) – 2

**Ans.** (C)

**Sol.** Sulphur atom in ground state



sulphur atom in excited state



Due to presence of six unpaired electrons, it can form maximum of six bonds, so covalency is six.

**Q.7** The formula of sulphur molecule is –

- (A) S<sub>2</sub> (B) S<sub>4</sub> (C) S<sub>6</sub> (D) S<sub>8</sub>

**Ans.** (D)

**Sol.** Sulphur atom in S<sub>8</sub> molecule is in sp<sup>3</sup> hybridization state and involves both bonding and non bonding pairs of electrons.

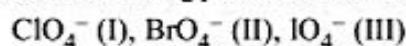
**Q.8** Which of the following is a false statement-

- (A) Halogens are strong oxidizing agent (B) Halogens show only (–1) oxidation state  
(C) HF molecules form intermolecular H-bonds (D) Fluorine is highly reactive

**Ans.** (B)

**Sol.** Fluorine, being most electronegative element, always show the oxidation state of –1. Other halogens can show higher positive oxidation state in addition to negative oxidation of –1.

**Q.9** Consider the following perhalate ion in acidic medium

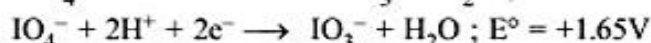
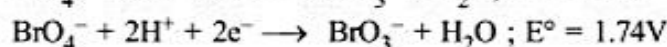
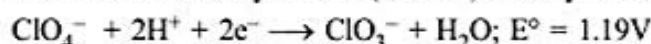


Arrange these in the decreasing order of oxidizing power.

- (A) I > II > III (B) I > III > II (C) II > I > III (D) II > III > I

**Ans.** (D)

**Sol.** Standard reduction potential (in volts) of the perhalate ions are gives as below –



more the standard reduction potential, the more is tendency of perhalite ion to undergo reduction and more stronger it will be an oxidizing agent.

**Q.10** Which of the following reactions will give bleaching powder –

- (A)  $\text{CaCl}_2 + \text{H}_2\text{O}$  (B)  $\text{CaO} + \text{HCl}$  (C)  $\text{Ca(OH)}_2 + \text{Cl}_2$  (D)  $\text{ClO}_2 + \text{Ca(OH)}_2$

**Ans.** (C)

**Sol.**  $\text{Ca(OH)}_2 + \text{Cl}_2 \longrightarrow \text{CaOCl}_2 + \text{H}_2\text{O}$   
Slaked lime

**Q.11** The boiling point and melting point of inert gases are –

- (A) Low (B) High (C) Very high (D) Very low

**Ans.** (D)

**Sol.** Due to very weak, Vander Waals forces.

**Q.12** The ease of liquefaction of noble gases increases in the order –

- (A)  $\text{He} < \text{Ne} < \text{Ar} < \text{Kr} < \text{Xe}$  (B)  $\text{Xe} < \text{Kr} < \text{Ne} < \text{Ar} < \text{He}$   
(C)  $\text{Kr} < \text{Xe} < \text{He} < \text{Ne} < \text{Ar}$  (D)  $\text{Ar} < \text{Kr} < \text{Xe} < \text{Ne} < \text{He}$

**Ans.** (A)

**Sol.** As size increases, Vander Waals forces also increases.

**Q.13** The statement, which prompted Neil Bartlett to prepare the first noble gas compound was –

- (A) Xe-F bond has high bond energy  
(B)  $\text{F}_2$  has exceptionally low bond energy  
(C)  $\text{PtF}_6$  is a strong oxidant  
(D)  $\text{O}_2$  molecule and Xe atom have very similar ionization energies.

**Ans.** (D)

**Sol.** Both Xe and  $\text{O}_2$  have comparable ionisation energies.

$\text{Xe} \longrightarrow \text{Xe}^+ + \text{e}^-$  ionisation energy = 1,170 kJ/mol

$\text{O}_2 \longrightarrow \text{O}_2^+ + \text{e}^-$  ionisation energy = 1,175 kJ/mol

**Q.14** Which of the following halides is most acidic ?

- (A)  $\text{PCl}_3$  (B)  $\text{SbCl}_3$  (C)  $\text{BiCl}_3$  (D)  $\text{CCl}_4$

**Ans.** (A)

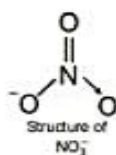
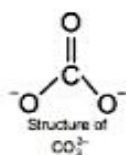
**Sol.** In  $\text{CCl}_4$ , carbon atom does not have d-orbitals to accommodate a lone pair of electrons and hence is not a Lewis acid. In  $\text{PCl}_3$ ,  $\text{SbCl}_3$ ,  $\text{BiCl}_3$  centre atom has empty d-orbitals but electronegativity of P is maximum, hence  $\text{PCl}_3$  is strongest acid.

**Q.15** Which of the following are isoelectronic and isostructural ?

- (A)  $\text{NO}_3^-$ ,  $\text{CO}_3^{2-}$  (B)  $\text{SO}_3$ ,  $\text{NO}_3^-$  (C)  $\text{ClO}_3^-$ ,  $\text{CO}_3^{2-}$  (D)  $\text{CO}_3^{2-}$ ,  $\text{SO}_3$

**Ans.** (A)

**Sol.**  $\text{NO}_3^-$  and  $\text{CO}_3^{2-}$  both have same number of electrons (32 electrons) and central atom in each being  $\text{sp}^2$  hybridized.



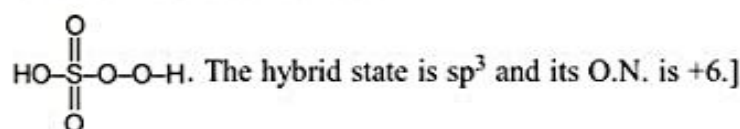
$\text{SO}_3 = 40$  electrons  
 $\text{ClO}_3^- = 42$  electrons

**Q.16** What is the hybrid state and oxidation state of sulphur in Caro's acid ?

- (A)  $\text{sp}^2$ , +10      (B)  $\text{sp}^3$ , +10      (C)  $\text{sp}^2$ , +6      (D)  $\text{sp}^3$ , +6

**Ans.** (D)

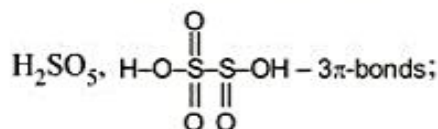
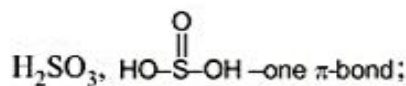
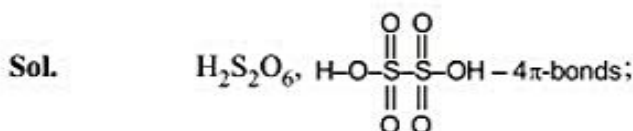
**Sol.** The structure of Caro's acid is



**Q.17** Identify the correct sequence of increasing number of  $\pi$ -bonds in structures of the following molecules—

- (i)  $\text{H}_2\text{S}_2\text{O}_6$       (ii)  $\text{H}_2\text{SO}_3$       (iii)  $\text{H}_2\text{S}_2\text{O}_5$   
 (A) I, II, III      (B) II, III, I      (C) II, I, III      (D) I, III, II

**Ans.** (B)

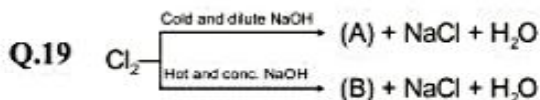
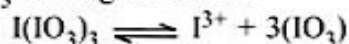


**Q.18**  $\text{I}_4\text{O}_9$  is an —

- (A) covalent bond      (B) coordinate compound  
 (C) ionic compound      (D) double salt

**Ans.** (C)

**Sol.**  $\text{I}_4\text{O}_9$  is actually  $\text{I}(\text{IO}_3)_3$  which gets ionised.



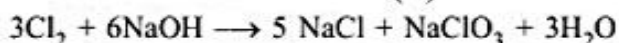
Compounds (A) and (B) are —

- (A)  $\text{NaClO}_3$ ,  $\text{NaClO}$     (B)  $\text{NaOCl}_2$ ,  $\text{NaOCl}$     (C)  $\text{NaClO}_4$ ,  $\text{NaClO}_3$     (D)  $\text{NaOCl}$ ,  $\text{NaClO}_3$

**Ans.** (D)



Cold and dil. (A)



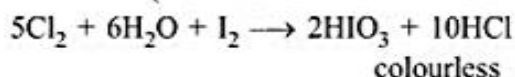
Hot and conc. (B)

**Q.20** When chlorine water is added to an aqueous solution of sodium iodide in the presence of chloroform, a violet colouration is obtained. On adding more of chlorine water and vigorous shaking, the violet colour disappears. This shows the conversion of.....into.....

- (A)  $I_2$ ,  $HIO_3$       (B)  $I_2$ ,  $HI$       (C)  $HI$ ,  $HIO_3$       (D)  $I_2$ ,  $HIO$

**Ans. (A)**

**Sol.**  $\text{Cl}_2 + 2\text{NaI} \longrightarrow 2\text{NaCl} + \text{I}_2$   
(Violet colouration in chloroform)

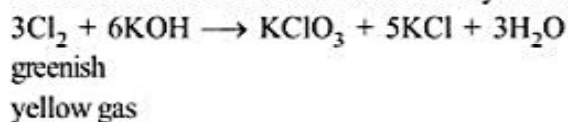


**Q.21** A greenish yellow gas reacts with an alkali hydroxide to form a halate which can be used in fireworks and safety matches. The gas and the halate are –

- (A)  $\text{Br}_2$ ,  $\text{KBrO}_3$       (B)  $\text{Cl}_2$ ,  $\text{KClO}_3$       (C)  $\text{I}_2$ ,  $\text{NaIO}_3$       (D)  $\text{I}_2$ ,  $\text{KIO}_3$

**Ans. (B)**

**Sol.** The halate used in fireworks and safety matches is  $\text{KClO}_3$ . Thus, the gas is  $\text{Cl}_2$ .

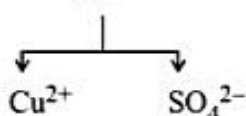
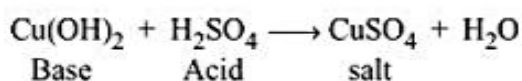




## QUALITATIVE ANALYSIS

**Analysis of substance is carried out in order to establish its qualitative and quantitative chemical composition.** Qualitative analysis deals with identifying the components of a substance. Inorganic salts are formed due to neutralization of acids and bases. So a salt comprises of two parts a cation or basic radical contributed by the base and an anion or acidic radical contributed by an acid.

A charged atom or groups of atoms which participates in chemical reactions.



(1) Basic radical

(2) Acidic radical

*	Positive radical	–	Basic radical
*	Negative radical	–	Acid radical

- (1) **Basic radical or cation :** It is the radical having positive charge. The magnitude of charge depends upon the base in which it is in combination with  $\text{OH}^-$  ions or formally of the basic oxide.  $\text{Pb}^{+2}$ ,  $\text{Cu}^{+2}$ ,  $\text{Al}^{+3}$ ,  $\text{Fe}^{+3}$ ,  $\text{Zn}^{+2}$ ,  $\text{Ni}^{+2}$ ,  $\text{Ca}^{+2}$ ,  $\text{Ba}^{+2}$ ,  $\text{Mg}^{+2}$ ,  $\text{NH}_4^+$
- (2) **Acid radical or Anion :** It is the radical having negative charge. The magnitude of charge depends upon the acid in which it is in combination with hydrogen.  $\text{CO}_3^{2-}$ ,  $\text{S}^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$

**Qualitative analysis :** Involves the detection and identification of these radicals in salts whether single salts or double salts, or detection of radicals in mixture of salts or even radicals present in common fertilizers. Qualitative analysis is a valuable tool in industries. However in laboratories semi Micro analysis is performed.

There are separate 'procedures for detecting cations and anions, therefore qualitative analysis is studied under cation analysis and anion analysis.

Qualitative analysis deals with the identification of various constituents present in a chemical mixture. The systematic procedure involves:

1. **Preliminary tests**
  - a. Physical appearance
  - b. Dry heating test
  - c. Charcoal cavity test
  - d. Flame test
  - e. Borax bead test
2. **Indicatory tests**
  - a. Dilute acid tests
  - b. Concentrated acid test
3. **Confirmatory tests**
  - a. Physical examination
  - b. Gas evolved on heating or by adding any reagent
  - c. Analysis of acid radicals
  - d. Analysis of basic radicals

# 1. Preliminary tests

- (a) **Physical appearance :** The physical examination of the unknown mixture involves the study of solubility colour, smell and density.

Following salts are soluble in water:

	Soluble	Insoluble
(i)	All the halides ( $X^- = \text{Cl}, \text{Br}, \text{I}$ ) are soluble in water Except Ag, Cu, Hg, Pb,	All the $\text{CO}_3^{2-}$ , $\text{C}_2\text{O}_4^{2-}$ , $\text{S}^{2-}$ , $\text{SO}_3^{2-}$ are insoluble in water. Except alkyl metal
(ii)	All nitrates	<b>Note :</b> $\text{FeC}_2\text{O}_4$ is soluble in water
(iii)	All nitrites except $\text{AgNO}_2$	
(iv)	All sulphate are soluble in water Except Ag, Sr, Ba, Pb, Hg, Ca, Sn	
(v)	All the acetates ( $\text{CH}_3\text{COO}^-$ ) are soluble in water. Except Ag, Hg	

	Experiment	Observation	Inference
(a)	Smell Take a pinch of the salt between your fingers and rub with a drop of water	Ammonical smell Vinegar like smell Smell like that of rotten eggs	$\text{NH}_4^+$ $\text{CH}_3\text{COO}^-$ $\text{S}^{2-}$
(b)	Density	(i) Heavy (ii) Light fluffy powder	Salt of $\text{Pb}^{2+}$ or $\text{Ba}^{2+}$ Carbonate salts
(c)	Deliquescence	Salt absorbs moisture and becomes paste like	(i) If coloured may be $\text{Cu}(\text{NO}_3)_2$ , $\text{FeCl}_3$ (ii) If colourless, may be $\text{Zn}(\text{NO}_3)_2$ , chlorides of $\text{Zn}^{2+}$ , $\text{Mg}^{2+}$ etc.
(d)	Colour	Blue or Bluish green Greenish Light Green Dark brown Pink, Violet Light pink, flesh colour  White	$\text{Cu}^{2+}$ or $\text{Ni}^{2+}$ $\text{Ni}^{2+}$ $\text{Fe}^{2+}$ $\text{Fe}^{3+}$ $\text{Co}^{2+}$ $\text{Mn}^{2+}$  Shows the absence of $\text{Cu}^{2+}$ , $\text{Ni}^{2+}$ , $\text{Fe}^{2+}$ , $\text{Fe}^{3+}$ , $\text{Mn}^{2+}$ , $\text{Co}^{2+}$

**(b) Dry heating test:**

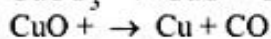
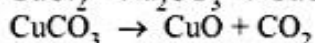
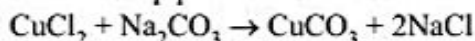
On heating a small amount of mixture in a dry test tube, quite valuable information can be generated by carefully performing and noting the observations here. On heating some salts undergo decomposition thus evolving the gases or may undergo characteristic changes in the colour of residue.

Observation	Inference
<b>(1) Gas evolved</b>	
(a) <b>Colourless and odourless gas</b> CO <sub>2</sub> gas - turns lime water milky	CO <sub>3</sub> <sup>2-</sup>
(b) <b>Colourless gas with odour</b>	
(i) H <sub>2</sub> S gas - Smells like rotten eggs, turns lead acetate paper black.	Hydrated S <sup>2-</sup>
(ii) SO <sub>2</sub> gas - Characteristic suffocating smell, turns acidified potassium dichromate solution or paper green.	SO <sub>3</sub> <sup>2-</sup>
(iii) HCl gas - Pungent smell, white fumes with ammonia, white precipitate with silver nitrate solution.	Cl <sup>-</sup>
(iv) Acetic acid vapours - Characteristic vinegar like smell.	CH <sub>3</sub> COO <sup>-</sup>
(v) NH <sub>3</sub> gas - Characteristic smell, turns Nessler's solution brown.	NH <sub>4</sub> <sup>+</sup>
(c) <b>Coloured gases - Pungent smell</b>	
(i) NO <sub>2</sub> gas - Reddish brown, turns ferrous sulphate solution black.	NO <sub>2</sub> <sup>-</sup> or NO <sub>3</sub> <sup>-</sup>
(ii) Cl <sub>2</sub> gas - Greenish yellow, turns starch iodide paper blue.	Cl <sup>-</sup>
(iii) Br <sub>2</sub> vapours - Reddish brown, turns starch paper orange red.	Br <sup>-</sup>
(iv) I <sub>2</sub> vapour - Dark violet, turns starch paper blue.	I <sup>-</sup>
<b>(2) Sublimate formed</b>	
(a) White sublimate	NH <sub>4</sub> <sup>+</sup>
(b) Black sublimate accompanied by violet vapours	I <sup>-</sup>
(c) Steel grey, garlic odour	As
(d) Grey sublimate	Hg
(e) Yellow sublimate	S, As <sub>2</sub> S <sub>3</sub>
<b>(3) Fusion test</b> The mixture swells up into voluminous mass.	Alkali metals salts or salts containing water of crystallisation
<b>(4) Swelling</b> The mixture swells up into voluminous mass.	PO <sub>4</sub> <sup>3-</sup> , BO <sub>3</sub> <sup>3-</sup> indicated
<b>(5) Residue</b>	
(i) Yellow when hot, white when cold.	Zn <sup>2+</sup>
(ii) Brown when hot and yellow when cold	Pb <sup>2+</sup>
(iii) Original salt blue becomes white on heating	Hydrated CuSO <sub>4</sub> indicated
(iv) Coloured salt becomes brown or black on heating	Co <sup>2+</sup> , Fe <sup>2+</sup> , Fe <sup>3+</sup> , Cr <sup>3+</sup> , Cu <sup>2+</sup> , Ni <sup>2+</sup> , Mn <sup>2+</sup> indicated.



**(c) Charcoal Cavity Test**

The mixture is mixed with double of its amount of anhydrous sodium carbonate and placed in a charcoal block having a small cavity. The mass is moistened with a drop of water and heated in a reducing flame with a blow pipe. Metal salt is converted into metal via carbonate and oxide. E.g.,



The colour in the cavity bead or incrustation is observed.

S.No.	Observation	Inference
1.	Formation of metallic bead (i) Lustrous white, malleable (ii) Greyish white, marks paper (iii) White, does not mark paper (iv) Red	Ag Pb Sn Cu
2.	Incrustation with metal (i) White incrustation, brittle metal (ii) Yellow incrustation, brittle metal (iii) Yellow incrustation, malleable metal	Sb Bi Pb
3.	Incrustation without metal (i) White and yellow when hot (ii) Yellow and orange when hot (iii) Brown (iv) White (volatile, garlic odour)	ZnO, SnO BiO CdO As <sub>2</sub> O <sub>3</sub>

**(d) Flame Test**

A paste of salts and concentrated HCl is taken into the lower oxidising zone and colour imparted to the flame by salts is observed. The salts of group V ( $\text{Ba}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ) are identified by colours of the flame.

Colour of the flame	Inference
Greenish blue	Cu salt and $\text{BO}_3^{-3}$
Apple-green	Ba
Crimson-red	Sr
Brick-red	Ca
Golden-yellow	Na
Violet	K
Carmine-red	Li

**Important note**

- (1) Be & Mg don't give flame test due to high ionization potential.
- (2) Colourless white salt don't possess Cu, Ni, Co, Fe, Mn, Cr etc.
- (3) White substances which swells are alum, borate and phosphate.

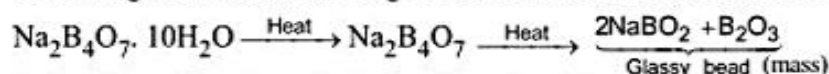


### Sublimation Action of a Substance and Colour

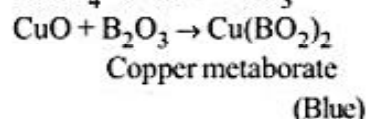
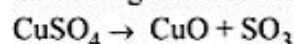
White	HgCl <sub>2</sub> , Hg <sub>2</sub> Cl <sub>2</sub> , As <sub>2</sub> O <sub>3</sub> , Sb <sub>2</sub> O <sub>3</sub>
Yellow	AlCl <sub>3</sub> and NH <sub>3</sub> halides
Brown	HgO, Hg(NO <sub>3</sub> ) <sub>2</sub>
Blue, Black and Violet	Iodides
Black	As, Sb, Hg sulphides and iodides.

#### (e) Borax Bead Test

On heating borax the colourless glass bead formed consists of sodium metaborate and boric anhydride.



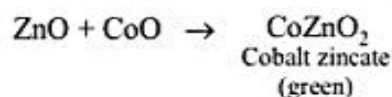
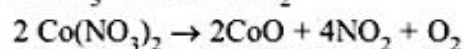
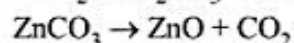
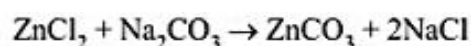
On heating with a coloured salt, the glassy bead forms a coloured metaborate in oxidising flame.



Metal	Oxidising - flame		Reducing - flame	
	Hot	Cold	Hot	Cold
Copper	Green	Blue	Colourless	Brown-red
Iron	Brown-yellow	Pale-yellow	Bottle green	Bottle green
Chromium	Green	Green	Green	Green
Cobalt	Blue	Blue	Blue	Blue
Nickel	Violet	Brown	Grey	Grey

#### (f) Cobalt Nitrate Charcoal Test

The mixture is mixed with double of its amount with sodium carbonate, placed in the charcoal cavity, and moistened with a drop of water and heated in an oxidising flame with the help of a blow pipe. After cooling, one or two drops of cobalt nitrate solution are added and the mass is again heated in the oxidising flame. Metal oxide combines with cobalt oxide (from cobalt nitrate) forming mixed oxide of characteristic colour.



Colour	Inference
Blue mass	Al
Green residue	Zn
Pink residue	Mg
Bluish green	Sn

## IDENTIFICATION OF ACIDIC RADICALS

**Group I :** This group consists of radical which are detected by dilute  $\text{H}_2\text{SO}_4$  or dilute  $\text{HCl}$ . These are (i) Carbonate, (ii) Sulphite, (iii) Sulphide, (iv) Acetate and (v) Nitrite

**Group II :** This group consists of radicals which are detected by concentrated  $\text{H}_2\text{SO}_4$ . These are (i) Chloride, (ii) Bromide, (iii) Iodide, (iv) Nitrate and (v) Oxalate

**Group III :** The radicals which do not give any characteristic gas with dilute and concentrated  $\text{H}_2\text{SO}_4$ . These are (i) Sulphate, (ii) Phosphate, (iii) Borate and (iv) Fluoride.

(A) **Observation of Dil.  $\text{HCl}$  /  $\text{H}_2\text{SO}_4$  + little amount of substance on slow heating.**

(1)  **$\text{CO}_3^{-2}$  (Carbonate)**

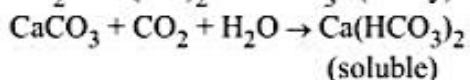
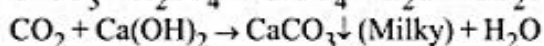
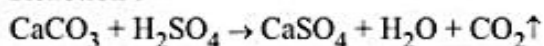
**Test/Observation/Analysis**

(i) Sharp bubbling of colourless gas ( $\text{CO}_2$ )

(ii) Gas turns milky to lime water.

(iii) On passing excess gas through lime water, milky colour disappears.

**Reaction :**



(2)  **$\text{SO}_3^{-2}$  (Sulphite)**

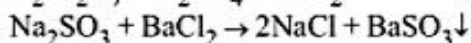
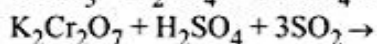
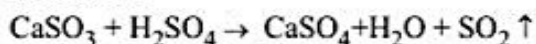
**Test/Observation/Analysis**

(i) Colourless gas ( $\text{SO}_2$ ) in which very unpleasant smell of burnt sulphur

(ii) Gas turns green to moist acidic  $\text{K}_2\text{Cr}_2\text{O}_7$  paper  $\text{K}_2\text{SO}_4 + \text{Cr(SO}_4)_3$  (green) +  $\text{H}_2\text{O}$

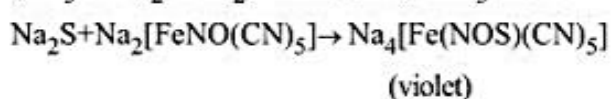
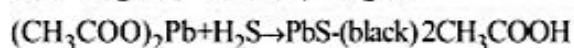
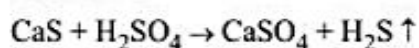
(iii) Sulphite gives white ppt. with  $\text{BaCl}_2$ , which is soluble in dil.  $\text{HCl}$

**Reaction :**

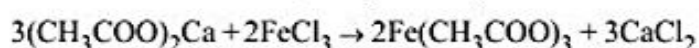
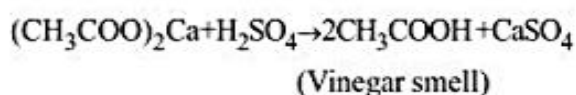


**(3) S<sup>2-</sup> (Sulphide)****Test/Observation/Analysis**

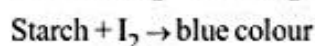
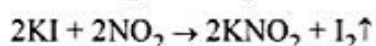
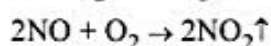
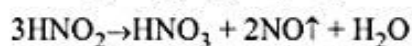
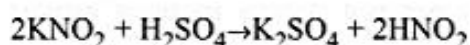
- (i) Colourless gas with rotten egg smell (H<sub>2</sub>S)
- (ii) Gas turns black to lead-acetate paper
- (iii) Sulphide turns violet colour to  
Sodium nitroprusside solution

**Reaction :****(4) CH<sub>3</sub>COO<sup>-</sup> (Acetate)****Test/Observation/Analysis**

- (i) Vinegar smell, acetate may be
- (ii) Acetate gives blood red colour with neutral  
FeCl<sub>3</sub> solution

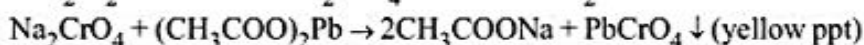
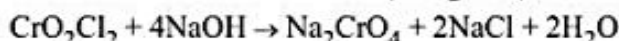
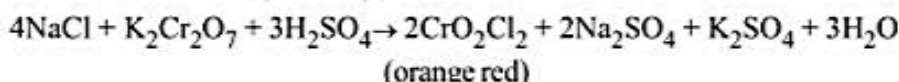
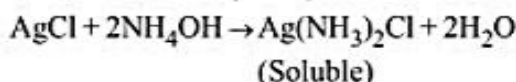
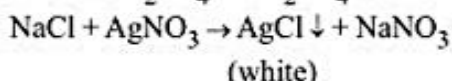
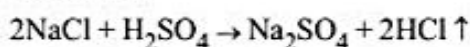
**Reaction :****(5) NO<sub>2</sub><sup>-</sup> (Nitrite)****Test/Observation/Analysis**

- (i) Red, brown NO<sub>2</sub> vapour comes out. Nitrite may be
- (ii) Gas turns blue to acidic KI starch paper

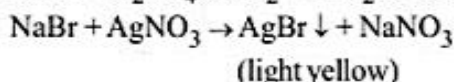
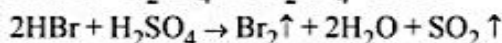
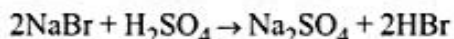
**Reaction :**

**(B) Observation of Conc.  $\text{H}_2\text{SO}_4$  + little amount of substance of slow heating****(6)  $\text{Cl}^-$  (Chloride)****Test/ observation/ Analysis**

- (i) Colourless fuming gas ( $\text{HCl}$ ) with fast smell
- (ii) Chloride gives white ppt. with  $\text{AgNO}_3$ , which is soluble in  $\text{NH}_4\text{OH}$
- (iii) Chromyl chloride test (**v.imp.**)
  - (a) Sodium chloride when heated with  $\text{K}_2\text{Cr}_2\text{O}_7$  & conc.  $\text{H}_2\text{SO}_4$  then orange red vapour of chromyl chloride  $\text{CrO}_2\text{Cl}_2$  comes out.  $\text{Hg}_2\text{Cl}_2$ ,  $\text{PbCl}_2$ ,  $\text{AgCl}$  does not give the positive chromyl chloride test.
  - (b) This vapour when passed with  $\text{NaOH}$  gives yellow solution ( $\text{Na}_2\text{CrO}_4$ )
  - (c) Acidic solution of  $\text{Na}_2\text{CrO}_4$  gives yellow ppt. with  $(\text{CH}_3\text{COO})_2\text{Pb}$

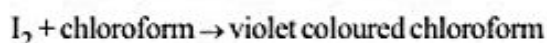
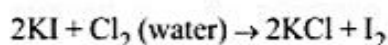
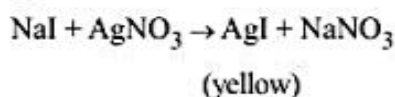
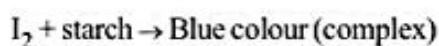
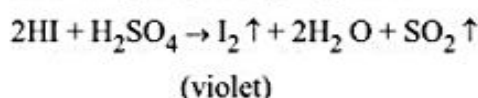
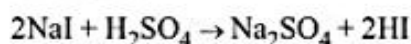
**Reaction :****(7)  $\text{Br}^-$  (Bromide)****Test/ observation/ Analysis**

- (i) Brown vapour comes out of  $(\text{Br}_2)\text{Br}^-$  or  $\text{NO}_3^-$  may be
- (ii) Bromides gives light yellow ppt. with  $\text{AgNO}_3$  which is partially soluble in  $\text{NH}_4\text{OH}$ .
- (iii) Brown vapour of  $\text{Br}_2$  when passed with  $\text{H}_2\text{O}$  gives brown colouration whereas  $\text{NO}_2$  vapour don't give any colour with  $\text{H}_2\text{O}$

**Reaction :****(8)  $\text{I}^-$  (Iodide)****Test/ observation/ Analysis**

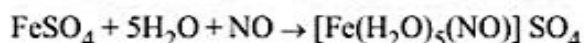
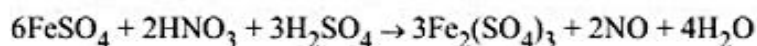
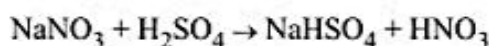
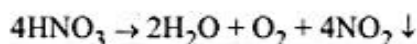
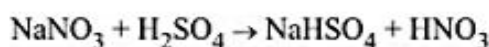
- (i) Dark violet fume of  $\text{I}_2$  comes out.
- (ii) Gives blue colouration with starch.
- (iii) Iodides gives yellow ppt. with  $\text{AgNO}_3$  which is insoluble in  $\text{NH}_4\text{OH}$
- (iv) Iodine with chloroform gives violet coloured chloroform



**Reaction :****(9)  $\text{NO}_3^-$  (Nitrate)****Test/ observation/ Analysis**

(i) Brown smoke comes out ( $\text{NO}_2$ )

(ii) Ring test (**v. imp.**) aq. solution of salt is mixed in fresh  $\text{FeSO}_4$  and conc.  $\text{H}_2\text{SO}_4$  is passed through corners of test tube, brown ring is formed. (brown ring of nitrosoferrous sulphate)

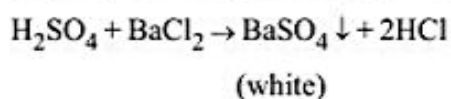
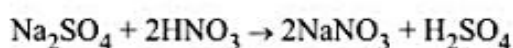
**Reaction :**

Solution

brown ring

**(10)  $\text{SO}_4^{2-}$  (Sulphate)****Test/ observation/ Analysis**

Small amount of substance + conc.  $\text{HNO}_3$  mixtures is heated & now adding  $\text{BaCl}_2$  white ppt comes which is insoluble in acid or base sulphate confirmed

**Reaction :**



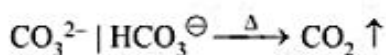
**Q.4** Salt A water soluble gives pink colour with phenolphthalene and salt B will not give pink colour with phenolphthalene but both salt give colourless or odourless gas (X) on heating, gas (X) gives white turbidity with Baryta water which disappear on passing excess of gas (X). Salt A and B are.

(A)  $\text{CO}_3^{2-}$  (B)  $\text{HCO}_3^-$  (C)  $\text{HSO}_3^-$  (D)  $\text{SO}_3^{2-}$

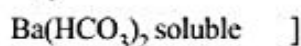
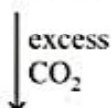
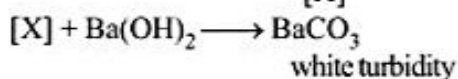
**Ans.** (A, B)

**[Sol.]** Salt A + HPh  $\longrightarrow$  Pink colour  
 $\text{CO}_3^{2-}$

Salt B + HPh  $\longrightarrow$  Hot pink colour  
 $\text{HCO}_3^-$



[X]



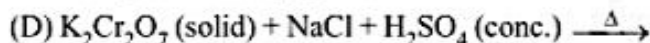
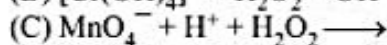
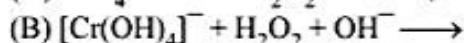
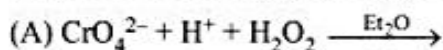
### Exercise

**Q.1** Borax bead test of salt (M) is performed, violet colour of the bead is obtained under oxidising flame. What is the oxidation state of the cation present in salt (M)?

(A) +7 (B) +4 (C) +2 (D) can't be predicted.

**Ans.** (D)

**Q.2** Which of the following reaction(s) is / are not redox reaction.



**Ans.** (A, D)

**Q.4**  $\text{SO}_2$  gas is passed through starch iodate solution in acidic medium and the resulting solution is

(A) Salmon red coloured precipitate  
 (B) Red compound of unknown composition  
 (C) Brown colour  
 (D) Deep blue solution

**Ans.** (D)

## TEST OF BASIC RADICALS

### I-Group

This group includes  $\text{Ag}^+$ ,  $\text{Pb}^{2+}$ , and  $\text{Hg}_2^{2+}$  (ous). The group reagent is dilute hydrochloric acid. The radicals are precipitated as their chlorides because the solubility product of these chlorides ( $\text{AgCl}$ ,  $\text{PbCl}_2$  and  $\text{Hg}_2\text{Cl}_2$ ) is less than the solubility of all other chlorides which thus remain in solution.

Radical	Test/ observation/ Analysis	Reaction
$\text{Pb}^{2+}$	$\text{Pb}^{2+}$ ion gives yellow ppt. with $\text{K}_2\text{CrO}_4$ & $\text{KI}$ soln. separately.	$\text{PbCl}_2 + \text{K}_2\text{CrO}_4 \rightarrow \text{PbCrO}_4(\text{yellow}) \downarrow + 2\text{KCl}$ $\text{PbCl}_2 + 2\text{KI} \rightarrow \text{PbI}_2 \downarrow (\text{yellow}) + 2\text{KCl}$
$\text{Hg}_2^{2+}$	$\text{Hg}_2^{2+}$ gives black ppt. with $\text{NH}_3$	$\text{Hg}_2\text{Cl}_2 + 2\text{NH}_4\text{OH} \rightarrow \text{Hg}(\text{NH}_2)\text{Cl} + \text{Hg} \downarrow + \text{NH}_4\text{Cl} + 2\text{H}_2\text{O}$
$\text{Ag}^+$	(i) $\text{AgCl}$ is soluble in $\text{NH}_4\text{OH}$ (ii) $\text{Ag}^+$ ion gives yellow ppt. with $\text{KI}$	$\text{AgCl} + 2\text{NH}_4\text{OH} \rightarrow [\text{Ag}(\text{NH}_3)_2]\text{Cl} + 2\text{H}_2\text{O}$ $\text{Ag}^+ + \text{I}^- \rightarrow \text{AgI} \downarrow (\text{yellow})$

**Note:**  $\text{PbCl}_2$  is soluble in hot water (but insoluble in cold water) Whereas insoluble in both  $\text{AgCl}$  &  $\text{HgCl}_2$

### II-Group

This group includes  $\text{Hg}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Bi}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$  (all in IIA),  $\text{As}^{3+}$ ,  $\text{Sb}^{3+}$ ,  $\text{Sn}^{2+}$  and  $\text{Sn}^{4+}$  (all in IIB).

The group reagent is hydrogen sulphide in presence of  $\text{HCl}$ . These radicals are precipitated as their sulphides, whereas the sulphides of other metals remain in solution because of their high solubility product.

$\text{HgS}$ ,  $\text{PbS}$ ,  $\text{Bi}_2\text{S}_3$  and  $\text{CuS}$  are black,  $\text{CdS}$ ,  $\text{As}_2\text{S}_3$  and  $\text{SnS}_2$  yellow,  $\text{SnS}$  brown, and  $\text{Sb}_2\text{S}_3$  is orange.

The function of  $\text{HCl}$  is to decrease ionisation of  $\text{H}_2\text{S}$  (due to common ion effect) so that only the solubility product of sulphides of II group radical is exceeded and not that of III, IV and V group. Hence III, IV and V group radicals are not precipitated by  $\text{H}_2\text{S}$  in the presence of  $\text{HCl}$ .

$\text{PbS}$  and  $\text{CdS}$  are precipitated only on dilution due to higher  $K_{sp}$ .

IIA and IIB group sulphides are separated by yellow ammonium sulphide  $(\text{NH}_4)_2\text{S}_x$  in which IIA group sulphides are insoluble whereas that of IIB are soluble forming thioalts.



Radical	Test/ observation/ Analysis	Reaction
<b>Hg<sup>+2</sup></b>	Adding Hg <sup>+2</sup> ion white ppt. obtained which turns black	$2\text{Hg}^{+2} + \text{SnCl}_2 \rightarrow \text{Sn}^{+4} + \text{Hg}_2\text{Cl}_2 \downarrow$ (white) $\text{HgCl}_2 + \text{SnCl}_2 \rightarrow \text{SnCl}_4 + 2\text{Hg} \downarrow$ (black)
<b>Pb<sup>+2</sup></b>	(i) In solution, Pb <sup>+2</sup> gives white ppt. with H <sub>2</sub> SO <sub>4</sub> (ii) In solution Pb <sup>+2</sup> ion gives yellow ppt. with K <sub>2</sub> CrO <sub>4</sub> & KI	$\text{Pb}^{+2} + \text{H}_2\text{SO}_4 \rightarrow \text{PbSO}_4 \downarrow + 2\text{H}^+$ (white) $\text{Pb}^{+2} + \text{Cr}_2\text{O}_4^{2-} \rightarrow \text{PbCrO}_4 \downarrow \text{ (yellow)}$ $\text{Pb}^{+2} + 2\text{I}^- \rightarrow \text{PbI}_2 \downarrow \text{ (yellow)}$
<b>Cu<sup>+2</sup></b>	(i) These ion gives dark blue colour with excess NH <sub>4</sub> OH (ii) Cu <sup>+2</sup> ion gives chocolate colour with K <sub>4</sub> Fe(CN) <sub>6</sub>	$\text{Cu}^{+2} + \text{NH}_4\text{OH} \rightarrow [\text{Cu}(\text{NH}_3)_4]^{+2} + \text{H}_2\text{O}$ (dark blue colour) $2\text{Cu}^{+2} + \text{K}_4\text{Fe}(\text{CN})_6 \rightarrow \text{Cu}_2[\text{Fe}(\text{CN})_6] \downarrow + 4\text{K}^+$ (chocolate or red brown ppt.)
<b>Bi<sup>+3</sup></b>	Bi <sup>+3</sup> ion gives white ppt. while adding water in HCl soln.	$\text{BiCl}_3 + \text{H}_2\text{O} \rightarrow \text{BiOCl} \downarrow + 2\text{HCl}$ (white bismuth oxychloride) $\text{BiCl}_3 + 3\text{Na}_2\text{SnO}_2 + 6\text{NaOH} \rightarrow$ (sodium stanite) $2\text{Bi} \downarrow + 3\text{Na}_2\text{SnO}_3 + 6\text{NaCl} + 3\text{H}_2\text{O}$ (black sodium stanate)
<b>Cd<sup>+2</sup></b>	(i) The yellow precipitate is dissolved in 50% HNO <sub>3</sub> . To the resulting solution, NH <sub>4</sub> OH is added slowly. A white ppt. appears which dissolve in excess of NH <sub>4</sub> OH. (ii) When H <sub>2</sub> S gas is passed in this solution a yellow ppt. appears	$3\text{Cds} + 8\text{HNO}_3 \rightarrow 3\text{Cd}(\text{NO}_3)_2 + 4\text{H}_2\text{O} + 2\text{NO} + 3\text{S}$ (50%) $\text{Cd}(\text{NO}_3)_2 + 2\text{NH}_4\text{OH} \rightarrow 2\text{NH}_4\text{NO}_3 + \text{Cd}(\text{OH})_2 \downarrow$ white ppt. $\text{Cd}(\text{OH})_2 + 2\text{NH}_4\text{OH} + 2\text{NH}_4\text{NO}_3 \rightarrow [\text{Cd}(\text{NH}_3)_4](\text{NO}_3)_2\text{aq.} + 4\text{H}_2\text{O}$ $[\text{Cd}(\text{NH}_3)_4](\text{NO}_3)_2 + \text{H}_2\text{S} \rightarrow \text{CdS} \downarrow + 2\text{NH}_4\text{NO}_3 + 2\text{NH}_3$ (yellow ppt.)

### III group

This group includes Fe<sup>3+</sup>, Al<sup>3+</sup>, and Cr<sup>3+</sup>. The group reagent is NH<sub>4</sub>OH and in presence of NH<sub>4</sub>Cl, the radicals are precipitated as their hydroxides. The function of NH<sub>4</sub>Cl is to suppress the ionisation of NH<sub>4</sub>OH so that only the III<sup>rd</sup> group radicals are precipitated, because the solubility product of III<sup>rd</sup> group hydroxides is less than that of IV and VI group hydroxides.

Excess of NH<sub>4</sub>Cl should be added, or else manganese will be precipitated in III group.

Radical	Test/ observation/ Analysis	Reaction
<b>Fe<sup>+3</sup>, Cr<sup>+3</sup> &amp; Al<sup>+3</sup></b>	These ion precipitates in the form of hydroxide on adding NH <sub>4</sub> Cl & NH <sub>4</sub> OH	$\text{Fe}^{+3} + 3\text{OH}^- \rightarrow \text{Fe}(\text{OH})_3 \text{ (red ppt.)}$ $\text{Cr}^{+3} + 3\text{OH}^- \rightarrow \text{Cr}(\text{OH})_3 \text{ (green ppt.)}$ $\text{Al}^{+3} + 3\text{OH}^- \rightarrow \text{Al}(\text{OH})_3 \text{ (white ppt.)}$

**Note :** In the analysis of III group, some drops of conc. HNO<sub>3</sub> are also added before oxidising Fe<sup>+2</sup> to Fe<sup>+3</sup>.

$\text{Al}^{+3}$	White ppt. of $\text{Al}(\text{OH})_3$ is soluble in $\text{NaOH}$	<b>Imp.</b> $\text{Al}(\text{OH})_3 + \text{NaOH} \rightarrow \text{NaAlO}_2 + 2\text{H}_2\text{O}$ (sodium metaaluminate)
$\text{Cr}^{+3}$	ppt. of $\text{Cr}(\text{OH})_3$ is soluble in $\text{NaOH} + \text{Br}_2$ water soln. in this soln. when $\text{BaCl}_2$ is added yellow	$\text{Br}_2 + \text{H}_2\text{O} \rightarrow 2\text{HBr} + \text{O}$ $2\text{Cr}(\text{OH})_3 + 4\text{NaOH} + 3\text{O} \rightarrow$ $2\text{Na}_2\text{CrO}_4 + 5\text{H}_2\text{O}$ ppt. is obtained $\text{Na}_2\text{CrO}_4 + \text{BaCl}_2 \rightarrow$ $\text{BaCrO}_4 \downarrow$ (yellow ppt.) $+ 2\text{NaCl}$
$\text{Fe}^{+3}$	(i) (a) Brown ppt. of $\text{Fe}(\text{OH})_3$ is soluble in $\text{HCl}$ (b) When $\text{KCNS}$ is added in this soln. soln. blood red colouration is obtained  (ii) In this soln., on adding $\text{K}_4[\text{Fe}(\text{CN})_6]$ , prussian blue colour is obtained	$\text{Fe}(\text{OH})_3 + 3\text{HCl} \rightarrow \text{FeCl}_3 + 3\text{H}_2\text{O}$ $\text{FeCl}_3 + 3\text{KCNS} \rightarrow \text{Fe}(\text{CNS})_3 + 3\text{KCl}$ (ferric thiocyanate) (blood red)  $4\text{FeCl}_3 + 3\text{K}_4[\text{Fe}(\text{CN})_6] \rightarrow$ $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3 + 12\text{KCl}$ (ferric ferrocyanide prussian blue)

#### IV group

This group includes  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Mn}^{2+}$ . The group reagent is hydrogen sulphide in ammonical solution. Radicals are precipitated as sulphides which are insoluble in  $\text{NH}_4\text{OH}$ .

$\text{CoS}$ ,  $\text{NiS}$  - Black

$\text{MnS}$  - Buff

$\text{ZnS}$  - White

The function of ammonium hydroxide is to increase the ionisation of  $\text{H}_2\text{S}$ .

Thus, an excess of sulphide ions will be available and hence the ionic product of IV group sulphides exceeds their solubility product and precipitates will be obtained.

Radical	Test/ observation/ Analysis	Reaction
$\text{Zn}^{+2}$ , $\text{Mn}^{+2}$ $\text{Co}^{+2}$ , $\text{Ni}^{+2}$ $\text{Co}^{+2}$ , $\text{Ni}^{+2}$ $\text{Zn}^{+2}$ $\text{Mn}^{+2}$ $\text{Ni}^{+2}$	These ions in presence of $\text{NH}_4\text{OH}$ precipitate on passing $\text{H}_2\text{S}$ . Black ( $\text{CoS}$ , $\text{NiS}$ ) ppt., (soluble in aqua-regia) White ( $\text{ZnS}$ ) (soluble in $\text{HCl}$ ) Pink or buff ( $\text{MnS}$ ), soluble in $\text{HCl}$ In presence of $\text{NH}_4\text{OH}$ , Ni salt on reaction with dimethyl glyoxime (DMG) turns red ppt. of nickel dimethyl glyoxime $\rightarrow$ Nickel dimethyl glyoxime (red ppt)	$\text{MCl}_2 + \text{H}_2\text{S} \rightarrow \text{MS} \downarrow + 2\text{HCl}$  <b>V. Imp.</b> $\text{CH}_3-\text{C}=\text{NOH} + \text{NiCl}_2 + 2\text{NH}_4\text{OH}$ $\quad \quad \quad  $ $\quad \quad \quad \text{CH}_3-\text{C}=\text{NOH}$ $\rightarrow (\text{C}_4\text{H}_7\text{N}_2\text{O}_2)_2\text{Ni} \downarrow + 2\text{NH}_4\text{Cl} + 2\text{H}_2\text{O}$
$\text{Co}^{+2}$	Cobalt salt turns blue colouration with $\text{NH}_4\text{CNS}$	$\text{CoCl}_2 + 4\text{NH}_4\text{CNS} \rightarrow$ $(\text{NH}_4)_2[\text{Co}(\text{CNS})_4] + 2\text{NH}_4\text{Cl}$ (ammonium cobalt thiocyanate) (blue colour)
$\text{Zn}^{+2}$	In solution, $\text{Zn}^{+2}$ ion turns white ppt. with $\text{NaOH}$ which is soluble in excess $\text{NaOH}$	<b>V. Imp</b> $\text{Zn}^{+2} + 2\text{NaOH} \rightarrow \text{Zn}(\text{OH})_2 \downarrow$ (white) $+ 2\text{Na}$ $\text{Zn}(\text{OH})_2 + 2\text{NaOH} \rightarrow \text{Na}_2\text{ZnO}_2 + 2\text{H}_2\text{O}$
$\text{Mn}^{+2}$	(a) $\text{Mn}^{+2}$ ion gives pink ppt. with $\text{NaOH}$ (b) On heating turns black or brown	<b>V. Imp</b> $\text{Mn}^{+2} + 2\text{NaOH} \rightarrow \text{Mn}(\text{OH})_2 \downarrow + 2\text{Na}$ (Pink)  $\text{Mn}(\text{OH})_2 + \text{O} \xrightarrow{\Delta} \text{MnO}_2 + \text{H}_2\text{O}$ (brown and black)

## V group

This includes  $\text{Ba}^{2+}$ ,  $\text{Sr}^{2+}$  and  $\text{Ca}^{2+}$ . The group reagent is ammonium carbonate in the presence of  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{OH}$ . These are precipitated as carbonates which are insoluble in  $\text{NH}_4\text{OH}$ .

The function of ammonium chloride is to suppress the ionisation of  $\text{NH}_4\text{OH}$  and  $(\text{NH}_4)_2\text{CO}_3$  and thus check the precipitation of  $\text{Mg}(\text{OH})_2$  (along with V group carbonates) because the solubility product of  $\text{Mg}(\text{OH})_2$  and  $\text{MgCO}_3$  is high. Further  $\text{NH}_4\text{Cl}$  should also not be added in excess, as the high concentration of  $\text{NH}_4^+$  ions will decrease the ionisation of  $(\text{NH}_4)_2\text{CO}_3$  to such an extent that sufficient  $\text{CO}_3^{2-}$  ions may not be present and carbonates of this group of metals may not precipitate.

Radical	Test/ observation/ Analysis	Reaction
$\text{Ba}^{+2}$ , $\text{Sr}^{+2}$ , $\text{Ca}^{+2}$	On adding $(\text{NH}_4)_2\text{CO}_3$ , these precipitates in the form of carbonates, soluble in $\text{CH}_3\text{COOH}$	$\text{M}^{+2} + (\text{NH}_4)_2\text{CO}_3 \rightarrow \text{MCO}_3 + 2\text{NH}_4^+$ $\text{BaCO}_3, \text{CaCO}_3, \text{SrCO}_3$ (white)
$\text{Ba}^{+2}$	Gives $\text{Ba}^{+2}$ ion in solution (i) Yellow ppt. with $\text{K}_2\text{CrO}_4$ (ii) white ppt. with $(\text{NH}_4)_2\text{SO}_4$ (iii) white ppt. with $(\text{NH}_4)_2\text{C}_2\text{O}_4$	$\text{Ba}^{+2} + \text{K}_2\text{CrO}_4 \rightarrow \text{BaCrO}_4 \downarrow (\text{yellow}) + 2\text{K}^+$ $\text{Ba}^{+2} + (\text{NH}_4)_2\text{SO}_4 \rightarrow \text{BaSO}_4 \downarrow (\text{white}) + 2\text{NH}_4^+$ $\text{Ba}^{+2} + (\text{NH}_4)_2\text{C}_2\text{O}_4 \rightarrow \text{BaC}_2\text{O}_4 \downarrow (\text{white}) + 2\text{NH}_4^+$
$\text{Sr}^{+2}$	$\text{Sr}^{+2}$ ion with $(\text{NH}_4)_2\text{SO}_4$ gives white precipitate	$\text{Sr}^{+2}(\text{NH}_4)_2\text{SO}_4 \rightarrow \text{SrSO}_4 \downarrow + 2\text{NH}_4^+$ (white ppt.)
$\text{Ca}^{+2}$	$\text{Ca}^{+2}$ ion gives white ppt. only with $(\text{NH}_4)_2\text{C}_2\text{O}_4$	$\text{Ca}^{+2} + (\text{NH}_4)_2\text{C}_2\text{O}_4 \rightarrow \text{CaC}_2\text{O}_4 \downarrow + 2\text{NH}_4^+$ (white) $\text{Sr}^{+2} + (\text{NH}_4)_2\text{C}_2\text{O}_4 \rightarrow \text{SrC}_2\text{O}_4 \downarrow + 2\text{NH}_4^+$ (white ppt.)

Note : The order of that is same as above  $\text{Ba}^{+2}$ ,  $\text{Sr}^{+2}$ ,  $\text{Ca}^{+2}$

## VI Group

Radical	Test/ observation/ Analysis	Reaction
$\text{Mg}^{+2}$ Zero group/ $\text{NH}_4^+$	$\text{Mg}^{+2}$ ion gives white ppt. with $\text{NH}_4\text{OH}$ & $(\text{NH}_4)_2\text{HPO}_4$ (i) (a) All ammonium salts on reacting with base like $(\text{NaOH})$ , gives smell of $\text{NH}_3$ (b) Gas evolved $(\text{NH}_3)$ gives white fume with $\text{HCl}$ (c) On passing $\text{NH}_3$ in $\text{Hg}_2(\text{NO}_3)_2$ , black colour is obtained (b) Brown ppt. is obtained with nessler's reagent	$\text{Mg}^{+2} + (\text{NH}_4)_2\text{HPO}_4 + \text{NH}_4\text{OH} \rightarrow \text{MgNH}_4\text{PO}_4 \downarrow (\text{white}) + 2\text{NH}_4^+ + \text{H}_2\text{O}$ (a) $\text{NH}_4\text{Cl} + \text{NaOH} \rightarrow \text{NaCl} + \text{NH}_3 \uparrow + \text{H}_2\text{O}$ (b) $\text{NH}_3 + \text{HCl} \rightarrow \text{NH}_4\text{Cl} \uparrow (\text{white fume})$ (c) $\text{Hg}_2(\text{NO}_3)_2 + 2\text{NH}_3 \rightarrow \text{Hg} + \text{Hg}(\text{NH}_2)\text{NO}_3 + \text{NH}_4\text{NO}_3$ (black) $\rightarrow$ (d) $2\text{K}_2\text{HgI}_4 + 4\text{KOH} + \text{NH}_4\text{Cl} \rightarrow$ (Nessler's reagent) $\begin{array}{c} \text{NH}_2 \\   \\ \text{Hg} \\   \\ \text{O} \\   \\ \text{Hg} \\   \\ \text{I} \end{array} + 7\text{KI} + \text{KCl} \cdot 3\text{H}_2\text{O}$ (Iodide solution black or brown ppt.) millions base



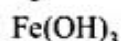
### Illustration

**Q.1** During group analysis, reddish brown ppt. is observed in group-III. What is the oxidation state of the metal present in the above precipitate.

- (A) +2 (B) +3 (C) both +2 and +3 (D) Can't be predicted

**Ans. (B)**

**[Sol.]** +3



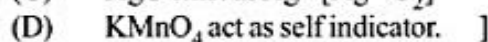
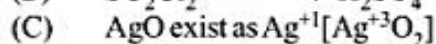
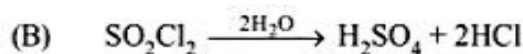
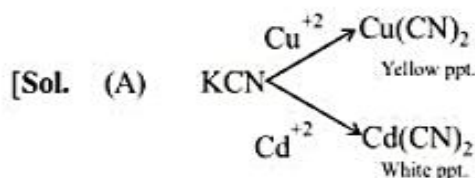
Reddish brown

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**Q.2** Which of the following statement is correct.

- (A) Using KCN solution  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  ion can not be distinguished  
 (B)  $\text{SO}_2\text{Cl}_2$  on hydrolysis produces two molecules of HCl and Caro's acid.  
 (C) The oxidation state of Ag in AgO is +2.  
 (D) No indicator is required in the estimation of  $\text{KMnO}_4$  using standard oxalic acid solution

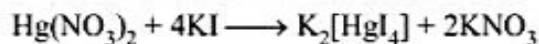
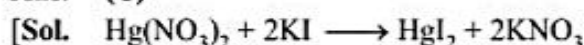
**Ans. (D)**



**Q.3** KI is added in excess into  $\text{Hg}(\text{NO}_3)_2$  solution. The observation is

- (A) Yellow ppt. of  $\text{HgI}_2$  (B) Scarlet red ppt. of  $\text{HgI}_2$   
 (C) Colourless solution of  $[\text{HgI}_4]^{2-}$  (D) None of these

**Ans. (C)**



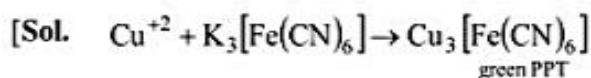
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**Q.4** Unknown solution of salt 'A'  $\xrightarrow{\text{K}_3[\text{Fe}(\text{CN})_6]}$  green ppt is obtained.

Which of the following radicals will be confirmed.

- (A)  $\text{Ni}^{2+}$  (B)  $\text{Cu}^{2+}$  (C)  $\text{S}_2\text{O}_3^{2-}$  (D)  $\text{SO}_3^{2-}$

**Ans. (B)**





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**Exercise**


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**Q.1** Select correct statement(s)

- (I) When excess  $\text{FeCl}_3$  solution is added to  $\text{K}_4[\text{Fe}(\text{CN})_6]$  solution in addition to  $\text{Fe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]^-$ ,  $\text{Fe}^{\text{II}}[\text{Fe}^{\text{III}}(\text{CN})_6]^-$  is also formed due to side redox reaction  
 (II) When  $\text{FeCl}_2$  is added to  $\text{K}_3[\text{Fe}(\text{CN})_6]$  solution, in addition to  $\text{Fe}^{\text{II}}[\text{Fe}^{\text{III}}(\text{CN})_6]^-$ ,  $\text{Fe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]^-$  is also formed due to side redox reaction.  
 (III)  $\text{Fe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]^-$  is paramagnetic while  $\text{Fe}^{\text{II}}[\text{Fe}^{\text{III}}(\text{CN})_6]^-$  is diamagnetic  
 (IV)  $\text{Fe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]^-$  is diamagnetic while  $\text{Fe}^{\text{II}}[\text{Fe}^{\text{III}}(\text{CN})_6]^-$  is paramagnetic  
 (A) I, II (B) III, IV (C) All (D) None

**Ans.** (A)

**Q.2** Which of the following compound is/are partially soluble or insoluble in  $\text{NH}_4\text{OH}$  solution

- (1)  $\text{Fe}(\text{OH})_3$  (2)  $\text{Ag}_2\text{CrO}_4$  (3)  $\text{Al}(\text{OH})_3$  (4)  $\text{Ag}_2\text{CO}_3$  (5)  $\text{Ni}(\text{OH})_2$   
 (A) 1, 3, 5 (B) 2, 3, 4 (C) 1, 3 (D) 2, 3, 5

**Ans.** (C)

**Q.3** The sulphide which is insoluble in both ammonium sulphide and  $\text{HNO}_3$  is

- (A)  $\text{Bi}_2\text{S}_3$  (B)  $\text{CuS}$  (C)  $\text{FeS}$  (D)  $\text{HgS}$

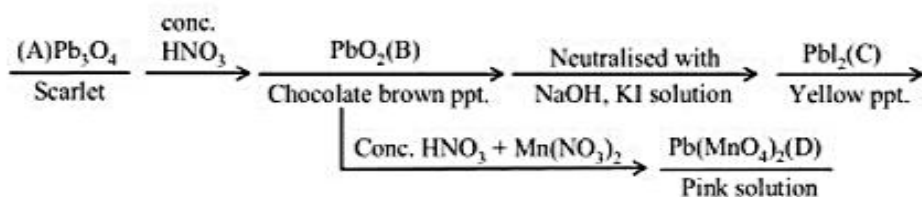
**Ans.** (D)

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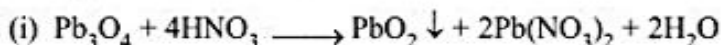
## SOLVED EXAMPLE

**Q.1** A scarlet compound A is treated with concentrated  $\text{HNO}_3$  to give a chocolate-brown precipitate B. The precipitate is filtered and the filtrate is neutralised with  $\text{NaOH}$ . Addition of  $\text{KI}$  to the resulting solution gives a yellow precipitate C. The precipitate B on warming with conc.  $\text{HNO}_3$  in the presence of  $\text{Mn}(\text{NO}_3)_2$  produces a pink-coloured solution due to the formation of D. Identify A, B, C, and D. Also, write the reaction sequence.

**Sol.** Since yellow precipitate (C) is obtained with  $\text{KI}$  and the pink-coloured solution is formed with concentrated  $\text{HNO}_3$  and  $\text{Mn}(\text{NO}_3)_2$ , the compound should be of Pb. We know that  $\text{Pb}_3\text{O}_4$  is a scarlet compound.



The equations are as follows:



**Q.2** A certain salt (X) gives the following tests:

(i) Its aqueous solution is alkaline to litmus.

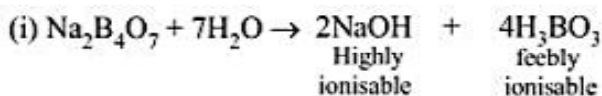
(ii) On strong heating, it swells to give a glassy material.

(iii) When concentrated sulphuric acid is added to a hot concentrated solution of (X), white crystals of an acid separate out.

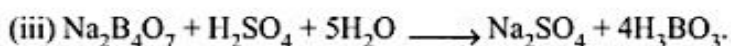
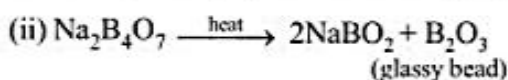
Identify (X) and write down the chemical equations for reactions at step (i), (ii), and (iii).

**Sol.** Since the aqueous solution of salt (X) is alkaline to litmus, it should be sodium or potassium salt. It swells to give a glassy material on heating, the salt (X) should be borax, that is,  $\text{Na}_2\text{B}_4\text{O}_7$  or  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ . It is further confirmed by the reaction of borax and concentrated  $\text{H}_2\text{SO}_4$  as it gives boric acid which is a white crystalline compound. Boric acid is a weak acid.

The reactions are as follows:



Since  $\text{NaOH}$  is highly ionisable and  $\text{H}_3\text{BO}_3$  is feebly ionisable, the solution is alkaline.



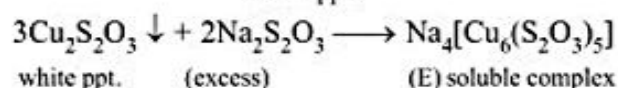
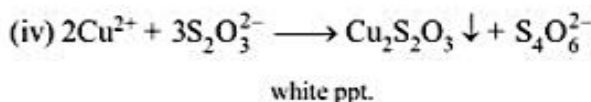
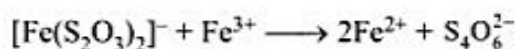
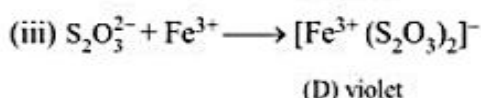
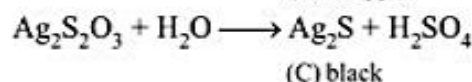
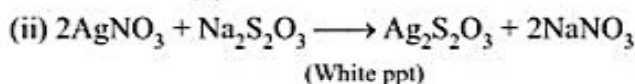
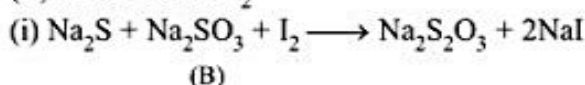
We know that  $\text{H}_3\text{BO}_3$  is a white crystalline compound and is a weak acid.

**Q.3**

- (i) An inorganic compound (A) is formed on passing a gas (B) through a conc. liquor containing  $\text{Na}_2\text{S}$  and sodium sulphite.
- (ii) On adding (A) into a dilute solution of silver nitrate a white precipitate appears which quickly changes into a black coloured compound (C).
- (iii) On adding two or three drops of  $\text{FeCl}_3$  into the excess of solution (A) a violet coloured compound (D) is formed. This colour disappears quickly.
- (iv) On adding a solution of (A) into the solution of cupric chloride, a white precipitate is first formed which dissolves on adding excess of (A) forming a compound (E).

Identify (A) to (E) and give chemical equations for the reactions at steps (i) to (iv).

**Sol.** The reactions indicate that the compound (A) is sodium thiosulphate. It is formed in step (i) by passing gas (B) which is either  $\text{I}_2$ .

**Q.4**

- (i) A blue coloured compound (A) on heating gives two of the products (B) & (C).
- (ii) A metal (D) is deposited on passing hydrogen through heated (B).
- (iii) The solution of (B) in  $\text{HCl}$  on treatment with the  $\text{K}_4[\text{Fe}(\text{CN})_6]$  gives a chocolate brown coloured precipitate of compound (E).
- (iv) (C) turns lime water milky which disappears on continuous passage of (C) forming a compound (F). Identify (A) to (F) and give chemical equations for the reactions at step (i) to (iv).

**Sol.**  $\text{A} = 2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ ,  $\text{B} = \text{CuO}$ ,  $\text{C} = \text{CO}_2$ ,  $\text{D} = \text{Cu}$ ,  $\text{E} = \text{Cu}_2[\text{Fe}(\text{CN})_6]$ ,  $\text{F} = \text{Ca}(\text{HCO}_3)_2$ .  
Azurite

**Q.5** A light bluish green crystalline compound responds to the following tests:

- (i) Its aqueous solution gives a brown precipitate or colouration with alkaline  $\text{K}_2[\text{HgI}_4]$  solution.
- (ii) Its aqueous solution gives a blue colour with  $\text{K}_3[\text{Fe}(\text{CN})_6]$  solution.
- (iii) Its solution in hydrochloric acid gives a white precipitate with  $\text{BaCl}_2$  solution.
- Identify the ions present and suggest the formula of the compound.



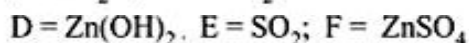
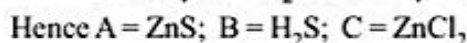
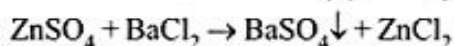
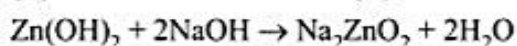
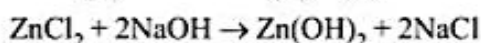
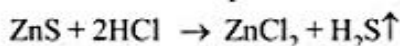




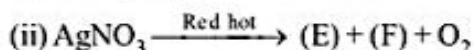
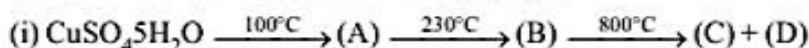
should be an amphoteric metal like Zn or Al. Again, solid F is soluble in HCl and gives a white precipitate with  $\text{BaCl}_2$ . Therefore, the anion must be  $\text{SO}_4^{2-}$  ion.

Substance A gives an offensive-smelling gas and, thus, the compound A may be  $\text{ZnS}$  or  $\text{Al}_2\text{S}_3$ . But,  $\text{Al}_2\text{S}_3$  on heating in air does not form  $\text{Al}_2(\text{SO}_4)_3$ .

$\therefore$  It is concluded that the compound A is  $\text{ZnS}$ . The chemical reactions are as follows:



**Q.8** Complete the following by identifying (A) to (F).



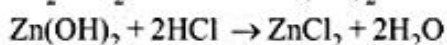
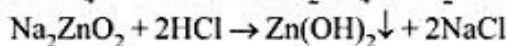
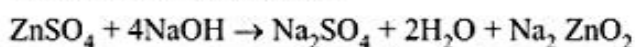
**Sol.**  $\text{A} = \text{CuSO}_4 \cdot \text{H}_2\text{O}$ ,  $\text{B} = \text{CuSO}_4$ ,  $\text{C} = \text{CuO}$ ,  $\text{D} = \text{SO}_3$ ,  $\text{E} = \text{Ag}$ ,  $\text{F} = \text{NO}_2$

**Q.9** An unknown solid mixture contains one or two of the following:  $\text{CaCO}_3$ ,  $\text{BaCl}_2$ ,  $\text{AgNO}_3$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{ZnSO}_4$ , and  $\text{NaOH}$ . The mixture is completely soluble in water and the solution gives pink colour with phenolphthalein. When 0.1 N HCl solution is gradually added to the above solution, a precipitate is produced which dissolves with further addition of the acid. What is /are present in the solid? Give equations to explain the appearance of the precipitate and its dissolution.

**Sol.** Since the mixture is completely soluble in water, the presence of  $\text{CaCO}_3$  is ruled out. Further, the solution of the mixture gives pink colour with phenolphthalein; therefore,  $\text{NaOH}$  is present in the mixture. Again, the precipitate is dissolved by adding HCl. This rules out the possibility of  $\text{BaCl}_2$ ,  $\text{AgNO}_3$ , or  $\text{Na}_2\text{SO}_4$ . It is because if  $\text{BaCl}_2$  is there, the precipitate of  $\text{Ba(OH)}_2$  should be formed in the presence of  $\text{NaOH}$  whereas the mixture is completely soluble. If  $\text{AgNO}_3$  is there, the precipitate of  $\text{AgCl}$  should be formed with HCl. There is no possibility to form precipitate with  $\text{Na}_2\text{SO}_4$ .

Now  $\text{ZnSO}_4$  may be the second compound of the mixture. Actually,  $\text{NaOH}$  is in excess in the mixture. Therefore, sodium zincate is formed in the solution which is soluble in water. On adding HCl in  $\text{Na}_2\text{ZnO}_2$ , a precipitate of  $\text{Zn(OH)}_2$  forms which dissolves in HCl to form  $\text{ZnCl}_2$ .

The reactions are as follows:



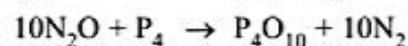
Hence, the mixture contains  $\text{NaOH}$  and  $\text{ZnSO}_4$ .

**Q.10** A colourless inorganic salt (A) decomposes completely at about  $250^{\circ}\text{C}$  to give only two products, (B) and (C), leaving no residue. The oxide (C) is a liquid at room temperature and neutral to moist litmus paper while the gas (B) is a neutral oxide. White phosphorus burns in excess of (B) to produce a strong white dehydrating agent. Write balanced equations for the reactions involved in the above process.

**Sol.** Since the colourless inorganic salt 'A' on heating gives no residue hence it should be ammonium salt. One of the products is oxide which is liquid at room temperature and neutral. Therefore, this oxide may be water. The second product is also neutral oxide. On the basis of above discussion, the compound 'A' may be  $\text{NH}_4\text{NO}_3$ . Its reactions are given below:



(A)                      (B)      (C)



$\text{P}_4\text{O}_{10}$  is strong dehydrating agent.

## d - BLOCK ELEMENTS

### TRANSITION ELEMENTS AND COMPLEXES

They are often called 'transition elements' because

- (i) They show's variable oxidation state in their compounds.
- (ii) Their outermost ( $n^{\text{th}}$ ) and as well as penultimate ( $n - 1$ ) shell is incomplete.
- (iii) Their position in the periodic table is between s-block and p-block elements

Typically, the transition elements have an incompletely filled d-level. Since Zn group has  $d^{10}$  configuration and are not considered as transition elements but they are d-block elements.

- (i) **The first transition series :** (3d series) involves the filling of 3d orbitals and has 10 elements from scandium ( $Z = 21$ ) to zinc ( $Z = 30$ )

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
$3d^1 4s^2$	$3d^2 4s^2$	$3d^3 4s^2$	$3d^5 4s^1$	$3d^5 4s^2$	$3d^6 4s^2$	$3d^7 4s^2$	$3d^8 4s^2$	$3d^{10} 4s^1$	$3d^{10} 4s^2$

- (ii) **The second transition series :** (4d series) involves the filling of 4d orbitals and has 10 elements from yttrium ( $Z = 39$ ) to cadmium ( $Z = 48$ ).

Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
$4d^1 5s^2$	$4d^2 5s^2$	$4d^4 5s^1$	$4d^5 5s^1$	$4d^5 5s^2$	$4d^6 5s^1$	$4d^7 5s^1$	$4d^9 5s^1$	$4d^{10} 5s^1$	$4d^{10} 5s^2$

- (iii) **The third transition series :** (5d series) involves the filling of 5d orbitals and has 10 elements. The first element of this series is lanthanum ( $Z = 57$ ). It is followed by 14 elements (lanthanides, involving filling of 4f orbitals). The next nine elements are from hafnium ( $Z = 72$ ) to mercury ( $Z = 80$ )

La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
$5d^1 6s^2$	$5d^2 6s^2$	$5d^3 6s^2$	$5d^4 6s^2$	$5d^5 6s^2$	$5d^6 6s^2$	$5d^7 6s^2$	$5d^9 6s^1$	$5d^{10} 6s^1$	$5d^{10} 6s^2$

- (iv) **The fourth transition series** is incomplete and contains only three elements  $_{89}\text{Ac}$ ,  $_{104}\text{Rf}$ ,  $_{105}\text{Ha}$ .

Zn (30) is  $[\text{Ar}] 4s^2 3d^{10}$

Cd (48) is  $[\text{Kr}] 5s^2 4d^{10}$

Hg (80) is  $[\text{Xe}] 6s^2 4f^{14} 5d^{10}$

These elements have completely filled  $(n-1)d$  subshell in their elementary as well as ionic state and so are not true transition metals. Their properties are quite different from those of transition metals.

Zn is used in galvanizing, in making alloys, in making white pigment and in rubber industry (ZnO acts as filler). Cd is used in nuclear reactors as moderators, in making NiCd storage cells and in making paints. Mercury is used in scientific equipments and in electrolytic cells. Several compounds of Hg are used in making antiseptics.



## GENERAL CHARACTERISTICS

(ii) Electronic configuration:  $(n-1)d^{1-10}ns^{1-2}$

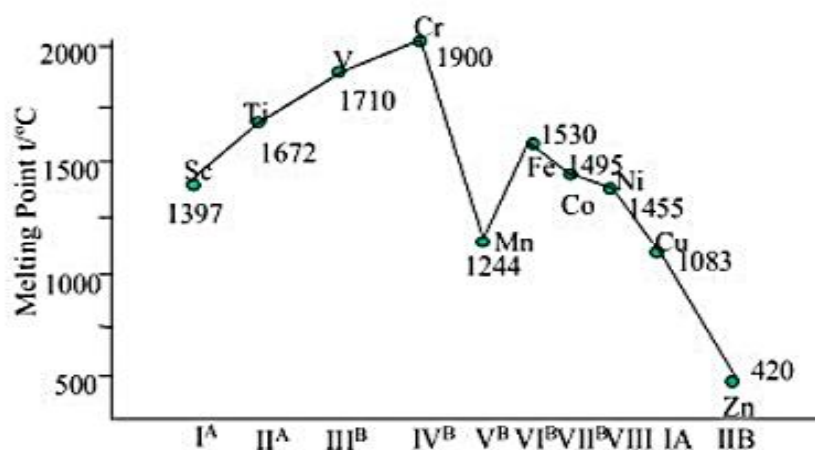
	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
others are				$4s^1$					$4s^1$	
as usual				$3d^5$					$3d^{10}$	

### (a) Metallic Character

- All the transition elements are metals, since the number of electrons in the outermost shell is very small being equal to 2.
- They are hard, malleable and ductile, except Hg which is liquid and soft.
- They exhibit all the three types of structures. Face Centred Cubic (fcc), Hexagonal Close packed (hcp) and Body Centred Cubic (bcc).
- Covalent and Metallic bonding both exist in the atom of transition metals.
- The presence of unfilled d- subshell favour covalent bonding, and metallic bonding is due to possession of one or two electron in outermost energy shell.
- These metals are good conductors of heat and electricity.

### (b) Melting and Boiling Points :

- The transition elements have very high melting & boiling points as compared to those of s & p block elements.
- The high melting and boiling point of transition metals are attributed to the stronger force that bind their atoms together.
- As the number of d- electron increases the number of covalent bond between the atoms are expected to increase up to Cr- Mo- W family where each of the d- orbital has only unpaired electrons and the opportunity for covalent sharing is greatest.
- In spite of presence of five unpaired electrons in Mn, the unexpected low melting and boiling is due to its complex structure it is unable to form metallic and covalent bonds.
- The absence of unpaired electron  $[(n-1)d^{10}4s^2]$  in Zn, Cd, & Hg is responsible for its low melting & boiling point.



Graphic representation m.p. of 3d - series elements



## (c) Atomic and Ionic Radii

Elements	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Atomic Radii (Å°)	1.44	1.32	1.22	1.18	1.14	1.17	1.16	1.15	1.27	1.25
Ionic radii (Å°) for $M^{2+}$	0.95	0.90	0.88	0.74	0.80	0.76	0.74	0.72	0.69	0.74
for $M^{3+}$	0.81	0.68	0.73	0.69	0.66	0.64	0.63	0.62	-	-
Metallic radii (Å°)	1.62	1.47	1.34	1.27	1.26	1.26	1.25	1.24	1.28	1.38

The value of these radii decreases generally, on moving from left to right in the period.

**Reason :**

- This is due to the fact that an increase in the nuclear charge tends to attract the electron cloud inwards.
- The radii for the elements from Cr to Cu are however very close to one another.
- The simultaneous addition of electron of 3d-level exercises the reverse effect by screening the outer 4s-electron from the inward pull of the nucleus.
- As a result of these two opposing effects, the atomic radii do not alter much on moving from Cr to Cu.
- The radii of  $M^{2+}$  ions, although some what smaller than that of  $Ca^{2+}$  ion ( $= 0.99 \text{ Å}^\circ$ ) are comparable with it.

**Oxides :**

- Thus Mo oxides of transition element should be similar to CaO in many ways, although some what less basic and less soluble in water.
- Similarly the Hydration energy of  $M^{2+}$  ion [ $Ti^{2+} \rightarrow Cu^{2+}$ ] are between 446 KCal to 597 KCal is some what greater than that of  $Ca^{2+}$  ion [ 395 K cal].

**Oxides of first row transition metals**

- Basic Oxides :  $Sc_2O_3$ ,  $TiO_2$ ,  $Ti_2O_3$ ,  $VO$ ,  $V_2O_3$ ,  $MnO$ ,  $FeO$ ,  $Fe_2O_3$ ,  $Fe_3O_4$ ,  $CoO$ ,  $NiO$ ,  $Cu_2O$ .
- Acidic oxides :  $V_2O_5$ ,  $CrO_3$ ,  $Mn_2O_7$ .
- Amphoteric oxides :  $TiO_2$ ,  $VO_3$ ,  $Cr_2O_3$ ,  $CrO_2$ ,  $Mn_2O_3$ ,  $Mn_3O_4$ ,  $MnO_2$ ,  $CuO$ .

## (d) Ionisation Potential

- The first ionisation potential of transitional elements lie between those of s & p block elements.
- The first ionization potential of all the transition elements lie between 6 to 10 ev.
- In case of transition elements the addition of the extra electron in the ( n- 1) d provides a screening effect which shields the outer ns electron from the inward pull of positive nucleus.
- Thus the effect of increasing nuclear charge & the shielding effect created due to the expansion of ( n- 1) d orbital oppose each other.
- On account of these counter affects, the ionisation potentials increases rather slowly on the moving in a period of the first transition series.
- The  $IE_1$  for the first four 3d - block elements ( Sc, Ti, V & Cr) differ only slightly from one another.
- Similarly the value of Fe, Co, Ni & Cu also are fairly close to one another.

Ionisation Potential (ev.)	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
IE <sub>1</sub>	6.56	6.83	6.74	7.43	7.43	7.90	7.86	7.63	7.72	9.39
IE <sub>2</sub>	12.91	13.69	14.26	16.95	15.69	16.21	17.08	18.21	20.34	18.00
IE <sub>3</sub>	24.79	27.52	29.35	31.0	23.34	30.69	33.54	35.21	36.88	39.78

(e) **Oxidation State**

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
			+1					+1	
	+2	+2	+2	+2	+2	+2	+2	+2	+2
+3	+3	+3	+3	+3	+3	+3	+3		
	+4	+4	+4	+4	+4	+4	+4		
		+5	+5	+5					
			+6	+6	+6				
				+7					

Colour: (aquated)

Sc<sup>3+</sup> → colourless

Ti<sup>4+</sup> → colourless

Ti<sup>3+</sup> → purple

V<sup>4+</sup> → blue

V<sup>3+</sup> → green

V<sup>2+</sup> → violet

Cr<sup>2+</sup> → blue

Cr<sup>3+</sup> → green

Mn<sup>3+</sup> → violet

Mn<sup>2+</sup> → light pink

Fe<sup>2+</sup> → light green

Fe<sup>3+</sup> → yellow

Co<sup>2+</sup> → pink

Ni<sup>2+</sup> → green

Cu<sup>2+</sup> → blue

Zn<sup>2+</sup> → colourless

(f) **Relative stability of various oxidation states :**

- (i) The relative stabilities of various oxidation states of 3d-series element can be correlated with the extra stability of 3d<sup>0</sup>, 3d<sup>5</sup> & 3d<sup>10</sup> configuration to some extent.

**Example-** Ti<sup>4+</sup> (3d<sup>0</sup>) is more stable than Ti<sup>3+</sup> (3d<sup>1</sup>)

Mn<sup>2+</sup> (3d<sup>5</sup>) is more stable than Mn<sup>3+</sup> (3d<sup>4</sup>).

- (ii) The higher oxidation state of 4d and 5d series element are generally more stable than those of the element of 3d series.

**Example -**

- (a) Mo<sup>vi</sup>O<sub>4</sub><sup>2-</sup>, Te<sup>vii</sup>O<sub>4</sub><sup>2-</sup> (4d-series element) & W<sup>vi</sup>O<sub>4</sub><sup>2-</sup>, Re<sup>vii</sup>O<sub>4</sub><sup>2-</sup> (5d-series elements) are more stable and in which the transition element concerned show their maximum oxidation state.
- (b) Cr<sup>vi</sup>O<sub>4</sub><sup>2-</sup> & Mn<sup>vii</sup>O<sub>4</sub><sup>2-</sup> (3d-series) are strong oxidizing agents.
- (iii) Strongly reducing states probably do not form fluorides or oxides, but may well form the heavier halides. Conversely, strong oxidizing state form oxides & fluoride, but not Bromide and Iodide.

**Example -**

- (a) V react with halogens to form  $\text{VF}_5$ ,  $\text{VCl}_4$ ,  $\text{VBr}_3$ , but doesn't form  $\text{VBr}_5$  or  $\text{VI}_5$  because in +5 oxidation state V is strong oxidizing agent thus convert  $\text{Br}^-$  &  $\text{I}^-$  to  $\text{Br}_2$  &  $\text{I}_2$  respectively, So  $\text{VBr}_3$  &  $\text{VI}_3$  are formed but not  $\text{VBr}_5$  &  $\text{VI}_5$ .
- (b) On the other hand  $\text{VF}_5$  is formed because  $\text{V}^{5+}$  ion unable to oxidize highly electronegative & small anion  $\text{F}^-$ .
- (c) Similarly highly electronegative and small  $\text{O}^{2-}$  ion formed oxides eg.  $\text{VO}_4^{3-}$ ,  $\text{CrO}_4^{2-}$  &  $\text{MnO}_4^-$  etc.
- (iv) All transition elements in their lower oxidation state like to form ionic compounds. Whereas in their higher oxidation state they generally formed covalent compound.

**Example-**

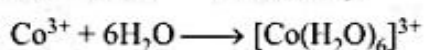
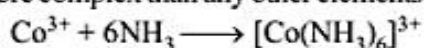
+2	+3	+4	+5	+6	+7
$\text{TiCl}_2$	$\text{TiCl}_3$	$\text{TiCl}_4$			
$\text{VCl}_2$	$\text{VCl}_3$	$\text{VCl}_4$	$\text{VOCl}_3$		
(Ionic, Less ionic basic) Amphoteric Covalent & Acidic, (Strong Lewis acid)					
$\text{TiO}$		$\text{Ti}_2\text{O}_3$		$\text{TiO}_2$	
$\text{VO}$		$\text{V}_2\text{O}_3$		$\text{V}_2\text{O}_5$	
$\text{CrO}$		$\text{Cr}_2\text{O}_3$		$\text{CrO}_3$	
$\text{MnO}$	$\text{Mn}_2\text{O}_3$	$\text{MnO}_2$	$\text{MnO}_3$	$\text{Mn}_2\text{O}_7$	
Ionic	Less Ionic			Acidic	
(Basic)	(Amphoteric)			(Covalent)	

**Formation of Complexes :**

By virtue of their small size, comparatively high nuclear or ionic charge and availability of vacant d-orbitals of suitable energy, these metals exert strong electrostatic attraction on the ligands. The species formed on interaction of metal and the ligand (or ligands) is known as a complex.

The transition metal ions form complexes because of the following reasons :

- (a) Their small cation size
- (b) High effective nuclear charge
- (c) Availability of vacant (n-1) d-orbitals of appropriate energy
- (d) The structure commonly found in such complex are linear (i.e. co-ordination number, C.N.=2), square planer (C.N.=4), tetrahedral (CN = 4) or octahedral (CN = 6).
- (e) Cobalt form more complex than any other elements



Metal ion	Ligand	C.N.	Complex ion
$\text{Ag}^+$	$\text{NH}_3$	2	$[\text{Ag}(\text{NH}_3)_2]^+$
$\text{Ni}^{+2}$	$\text{CN}^-$	4	$[\text{Ni}(\text{CN})_4]^{-2}$
$\text{Cu}^{2+}$	$\text{NH}_3$	4	$[\text{Cu}(\text{NH}_3)_4]^{+2}$
$\text{Fe}^{+2}$	$\text{CN}^-$	6	$[\text{Fe}(\text{CN})_6]^{-4}$



**(g) Magnetic properties**

- \* Matter, in general is associated with magnetic properties. Majority of substances are either paramagnetic or diamagnetic. A paramagnetic substance is one which is attracted into a magnetic field. Paramagnetism is mainly due to the presence of unpaired electrons in atoms or ions or molecules. Diamagnetic substance is one which is slightly repelled by a magnetic field.
- \*  $Ti^{+2} [Ar]3d^2$ ,  $Ti^{+3} [Ar]3d^1$ ,  $V^{+2}[Ar]3d^3$ ,  $Cr^{+3}[Ar]3d^3$   
As is evident most of the transition metal ions have unpaired electrons in their 'd' orbitals. Hence most of the transition metal ions are paramagnetic in nature. Transition metal ions having  $3d^0$  and  $3d^{10}$  configuration exhibit diamagnetic nature.
- \* An unpaired electron spins and as it is a charged particle, magnetic field is created due to its spinning.
- \* Each electron may, in fact, be considered as a micro magnet having a certain value of magnetic moment. The total magnetic moment of a substance is the resultant of the magnetic moments of all the individual electrons. Thus substances containing unpaired electrons get attracted towards the magnets exhibiting paramagnetic nature.
- \* The magnetic moment ( $\mu$ ) created due to spinning of unpaired electrons can be calculated by using  

$$\mu = \sqrt{n(n+2)} :$$
Where 'n' is the number of unpaired electrons in the metal ion.  

$$\mu = \text{Magnetic moment in Bohr Magnetons (B.M.)}$$
- \* The magnetic moment of diamagnetic substances will be zero.
- \* As the number of unpaired electrons increase the magnetic moment created goes on increasing and hence the paramagnetic nature also increases.
- \* Transition metal ions having  $d^5$  configuration will have maximum number of unpaired electrons therefore they will be maximum paramagnetic in nature.

**Variation of Magnetic moment of 3d- series**

Ions with configuration	Outer most configuration	Number of unpaired electron	Magnetic Moment $\mu$ B.M.
$Sc^{3+}$	$3d^0$	0	0
$Ti^{3+}, V^{4+}$	$3d^1$	1	1.75
$Ti^{2+}, V^{3+}$	$3d^2$	2	2.86
$V^{2+}, Cr^{3+}$	$3d^3$	3	3.86
$Cr^{3+}, Mn^{3+}$	$3d^4$	4	4.80
$Mn^{2+}, Fe^{3+}$	$3d^5$	5	5.95
$Fe^{2+}, Co^{3+}$	$3d^6$	4	5.0 – 5.5
$Co^{2+}$	$3d^7$	3	4.0 – 5.2
$Ni^{2+}$	$3d^8$	2	2.9 – 3.4
$Cu^{2+}$	$3d^9$	1	1.4– 2.2
$Zn^{2+}$	$3d^{10}$	0	0

**(h) Formation of Coloured Compounds :**

The transition metal ions have unpaired d-electrons, which on absorbing visible light can jump from one d-orbital to another i.e. intra d-d- transition take place. Thus when light falls certain visible wavelengths are absorbed. The reflected light appears coloured and gives the colour of compound. The ions having no d-d transitions are colourless.



**A - Factors affecting the colour of complex.**

The colour of a transition metal complex depend on-

- (i) The magnitude of energy difference between the two d- levels ( $\Delta_0$ ),
- (ii) An increase in the magnitude of  $\Delta_0$  decreases the wave length ( $\lambda$ ) of the light absorbed by the complexes.
- (iii) Thus with a decrease in the  $\lambda$  the colour of complex changes from Red  $\longrightarrow$  Violet.

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Oxidation Potential value (v) for $M \rightarrow M^{2+} + 2e^-$	-	1.60	1.20	0.91	1.18	0.44	0.28	0.25	0.34	0.76
$M \rightarrow M^{3+} + 3e^-$	2.10	-	-	0.74	-	-	-	-	-	-

**(i) Formation of interstitial compounds**

- (i) Small non metallic atom such as H, B, C, N etc. are able to occupy interstitial space of the lattice of the d-block elements to form combinations which are termed interstitial compounds.
- (ii) These are non-stoichiometric in nature and do not follow the common rule of valency.
- (iii) These interstitial compounds have similar chemical properties as the parent metal but differ appreciably in their physical properties such as density, hardness and conductivity.

**(j) Catalytic properties**

Many transition metals & their compounds have catalytic properties. Some common examples are-

- (a) In some cases the transition metals with their variable valency may form unstable intermediate compounds.
- (b) In other cases the transition metal provide a suitable reaction surface.
- (c) Enzymes are catalyst that enhance the rate of specific reactions. Some enzymes require the presence of metal ions as cofactors and these are called metalloenzymes.
  - (i)  $TiCl_3$  - Used as Ziegler - Natta catalyst in the production of polyethene.
  - (ii)  $V_2O_5$  - Convert  $SO_2$  to  $SO_3$  in the contact process for making  $H_2SO_4$ .
  - (iii)  $MnO_2$  - Used as a catalyst to decompose  $KClO_3$  to give  $O_2$ .
  - (iv) Fe - promoted iron is used in Haber- Bosch process for making  $NH_3$ .
  - (v)  $FeCl_3$  - Used for making  $CCl_4$  from  $CS_2$  &  $Cl_2$ .
  - (vi)  $FeSO_4$  &  $H_2O_2$  - Used as Fenton's reagent for oxidizing alcohol to aldehyde.
  - (vii) Pt.- used as a catalyst in the manufacture of  $H_2SO_4$ .
  - (viii) Ni - used as a catalyst in the hydrogenation of oils.
  - (ix)  $PdCl_2$  - Wacker process for converting  $C_2H_4 + H_2O + PdCl_2$  to  $CH_3CHO + 2HCl + Pd$ .
  - (x) Pt/ PtO- Adams catalyst, used for reduction.

**(k) Alloy formation**

- (i) Transition metals form a large number of alloys.
- (ii) d- block elements are quite similar in atomic size, the atom of one metal can substitute the atoms of other metal in its crystal lattices.
- (iii) Thus, on cooling a mixture solution of two or more transition metals, smooth solid, alloys are formed.
- (iv) Alloy containing mercury as one of the constituent elements are called amalgams.
- (v) The purpose of making alloy is to develop some useful properties which are absent in constituent element

## COMPOUNDS OF TRANSITION ELEMENTS

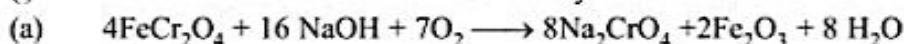
### (I) Potassium Dichromate ( $K_2Cr_2O_7$ )

#### (a) Preparation :

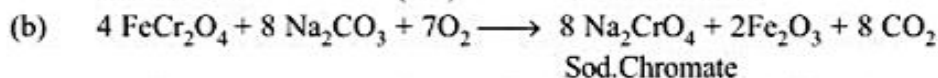
- (i) It is prepared from Chromite ore ( $FeCr_2O_4$ ).
- (ii) The preparation of  $K_2Cr_2O_7$  from chromite ore involve the following steps :

#### (A) Conversion of Chromite ore to Sodium Chromate :

- (i) The Chromite ore is fused with Sodium hydroxide or Sodium Carbonate in the presence of air.



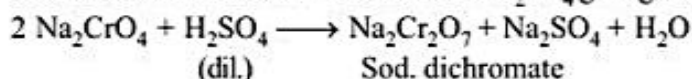
Chromite ore (Air) Sod. Chromate



Sod. Chromite is extracted with water & ferric oxide is left behind.

#### (B) Conversion of Sodium chromate to Sodium dichromate :

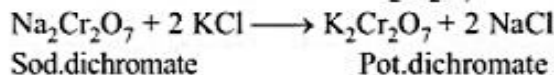
- (i) The Sod. chromite is acidified with dilute  $H_2SO_4$  giving its dichromate



- (ii) On concentration, the less soluble sulphate crystallises and is filtered out. The resulting solution contains Sod. dichromate.

#### (C) Conversion of Sod. dichromate to Pot. dichromate :

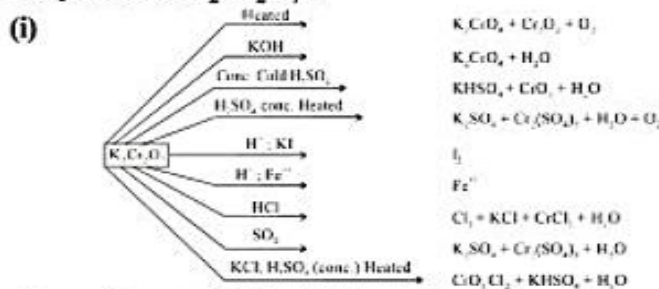
- (i) Hot concentrated solution of  $Na_2Cr_2O_7$  with KCl in equimolar proportion



#### Properties :

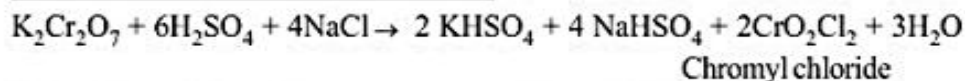
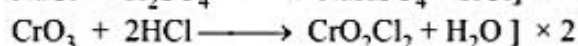
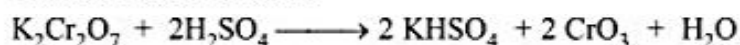
It is orange- red crystalline compound having melting point 670 K.

#### Properties of $K_2Cr_2O_7$ :

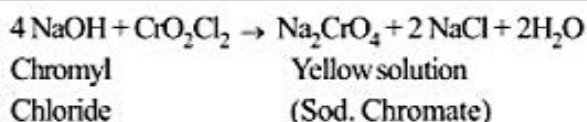
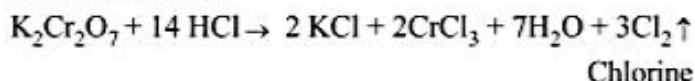


#### (ii) Chromyl Chloride Test :

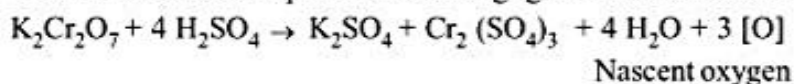
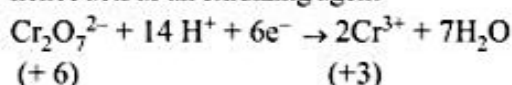
- (a) This is the test of Chloride



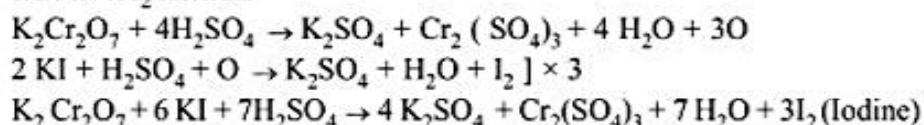
- (b) When Chromyl Chloride vapours are passed through NaOH solution, yellow coloured solution is obtained.

(iii) **Action with HCl :**(iv) **Oxidising character :**

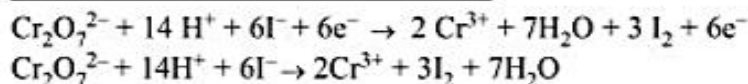
(A) The dichromates act. as powerful oxidizing agent in acidic medium.

(B) In term of electronic concept, the  $\text{Cr}_2\text{O}_7^{2-}$  ion take up electron in Acidic medium and hence acts as an oxidizing agent

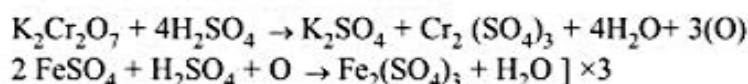
**Note :** Both  $\text{Na}_2\text{Cr}_2\text{O}_7$  &  $\text{K}_2\text{Cr}_2\text{O}_7$  are oxidizing agents but  $\text{K}_2\text{Cr}_2\text{O}_7$  is preferred since it is not hygroscopic and can be used as primary standard.

(C) Some oxidizing reactions of  $\text{K}_2\text{Cr}_2\text{O}_7$  are :(a) It liberate  $\text{I}_2$  from KI

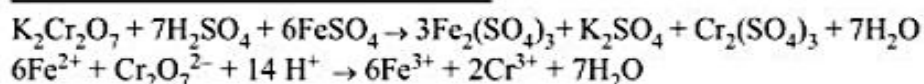
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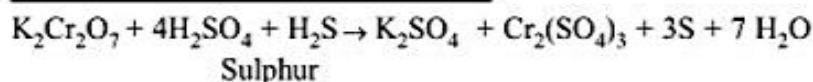
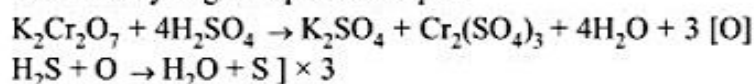
(b) It oxidises ferrous salts to ferric salts.



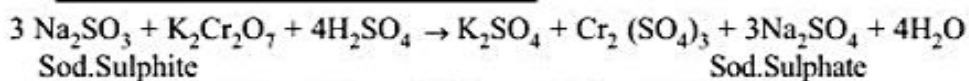
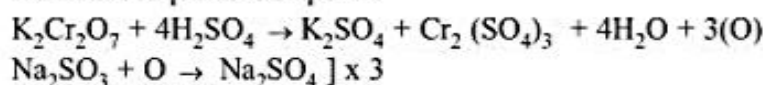
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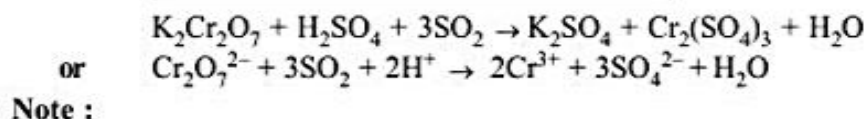
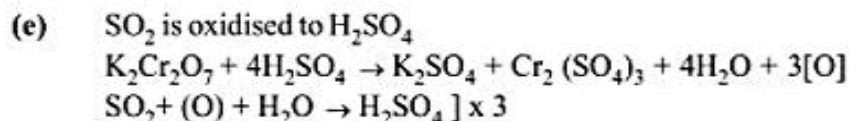
(c) It oxidises hydrogen sulphide to sulphur

or  $\text{H}_2\text{S} + \text{Cr}_2\text{O}_7^{2-} + 8 \text{H}^+ \rightarrow 2 \text{Cr}^{3+} + 3 \text{S} + 7 \text{H}_2\text{O}$ 

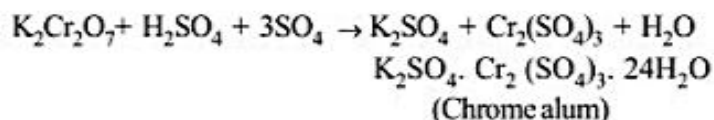
(d) It oxidises sulphites to sulphates

or  $3 \text{SO}_3^{2-} + \text{Cr}_2\text{O}_7^{2-} + 8 \text{H}^+ \rightarrow 3 \text{SO}_4^{2-} + 2 \text{Cr}^{3+} + 4 \text{H}_2\text{O}$

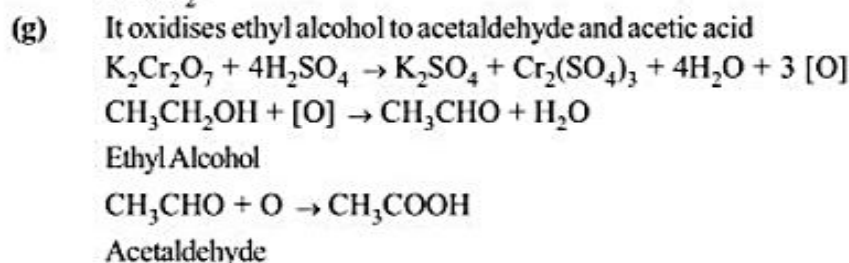




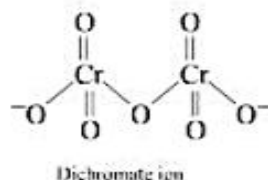
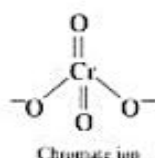
Note :



(f) Similarly, it oxidises, chlorides to chlorine, nitrites to nitrates, arsenites to arsenates thiosulphate to sulphate and sulphur ( $\text{S}_2\text{O}_3^{2-} + \text{O} \rightarrow \text{SO}_4^{2-} + \text{S}$ ),  $\text{HBr}$  to  $\text{Br}_2$ ,  $\text{HI}$  to  $\text{I}_2$ .



#### Structure of Chromate and dichromate ions :



Uses : Potassium dichromate is used :

- As a volumetric reagent in laboratory for the estimation of ferrous ions, iodide ions etc.
- For the preparation of chrome yellow ( $\text{PbCrO}_4$ ), Chrome red ( $\text{PbCrO}_4 \cdot \text{PbO}$ ), Zinc yellow ( $\text{ZnCrO}_4$ ), Guggers green ( $\text{Cr}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ ), chromic acid ( $\text{CrO}_3$  - orange),  $\text{K}_3[\text{CrO}_8]$  (Red brown).
- In organic chemistry as oxidising agents.
- In photography for hardening gelatine films.

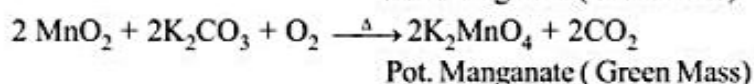
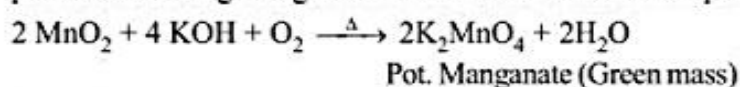
## 2. Potassium Permanganate ( $\text{KMnO}_4$ ) :

**Preparation :** Potassium Permanganate is prepared from mineral pyrolusite ( $\text{MnO}_2$ ).

The preparation involves the following steps.

### (A) Conversion of Pyrolusite ore to Potassium Manganate

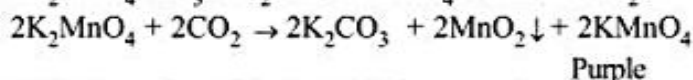
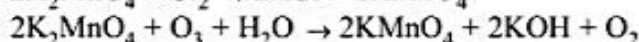
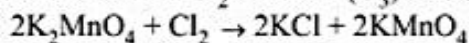
- (a) The pyrolusite ( $\text{MnO}_2$ ) is fused with caustic potash ( $\text{KOH}$ ) or potassium carbonate in presence of air to give a green mass due to the formation of potassium manganate.



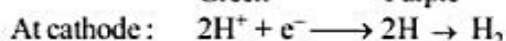
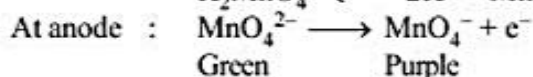
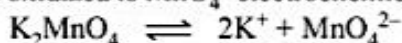


**(B) Oxidation of Potassium Manganate to Potassium permanganate :**

- (a) The fused mass is extracted with water and the solution is green ( $\text{MnO}_4^{2-}$ ). The solution is treated with  $\text{Cl}_2$  or ozone ( $\text{O}_3$ ) or  $\text{CO}_2$  to oxidize  $\text{K}_2\text{MnO}_4$  to  $\text{KMnO}_4$ .



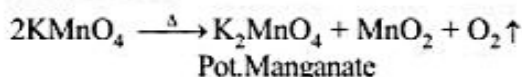
- (b)  $\text{MnO}_4^{2-}$  can be oxidized to  $\text{MnO}_4^-$  electrochemically at anode.

**Properties :**

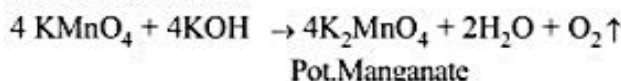
- (A) It is a dark violet crystalline solid having a metallic lustre. It has M.P. 523 K.

- (B) It is fairly soluble in water giving a purple solution.

- (C) Action of heat

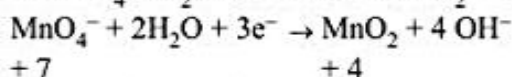


- (D) Action of alkalis :

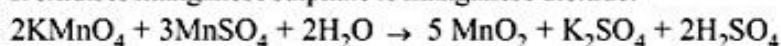


- (E) **Oxidising character :** Potassium permanganate act as an oxidizing agent in neutral, alkaline and acidic solutions.

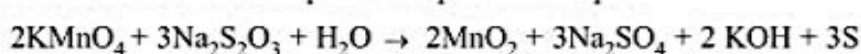
- (a) **In Neutral Medium :**  $\text{MnO}_2$  is formed

**Important reactions of Neutral  $\text{KMnO}_4$** 

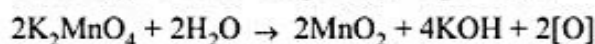
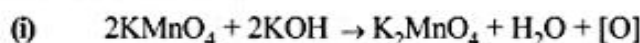
- (ii) It oxidises manganese sulphate to manganese dioxide.



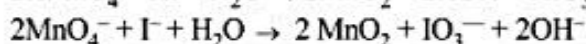
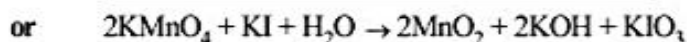
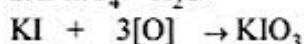
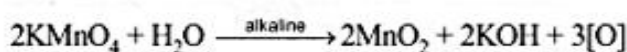
- (iii) It oxidises sodium thiosulphate to sulphate and Sulphur



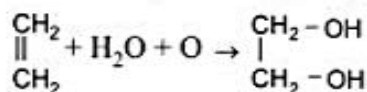
- (b) **Alkaline medium :**

**Important reactions of alkaline  $\text{KMnO}_4$  :**

- (i) It oxidises iodides to iodates in alkaline medium

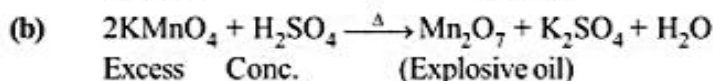
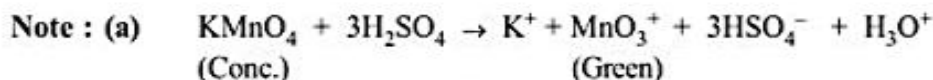


- (ii) Oxidises ethylene to ethylene glycol :

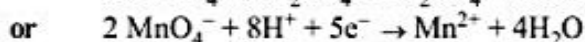
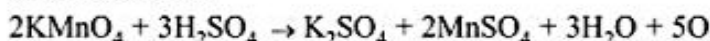


Ethylene Glycol

In alkaline medium it is called **Bayer's Reagent**

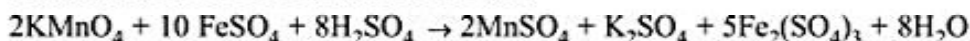


- (c) **Acidic solution :**

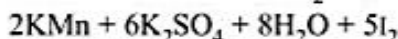


**Some of the important reactions of acidified  $\text{KMnO}_4$  are**

- (i) It oxidises acidified ferrous salt to ferric salts.



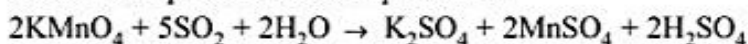
- (ii) It oxidises acidified KI to  $\text{I}_2$



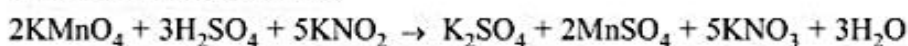
- (iii) It oxidises  $\text{H}_2\text{S}$  to Sulphur



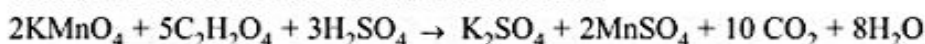
- (iv) It oxidises sulphur dioxide to sulphuric acid



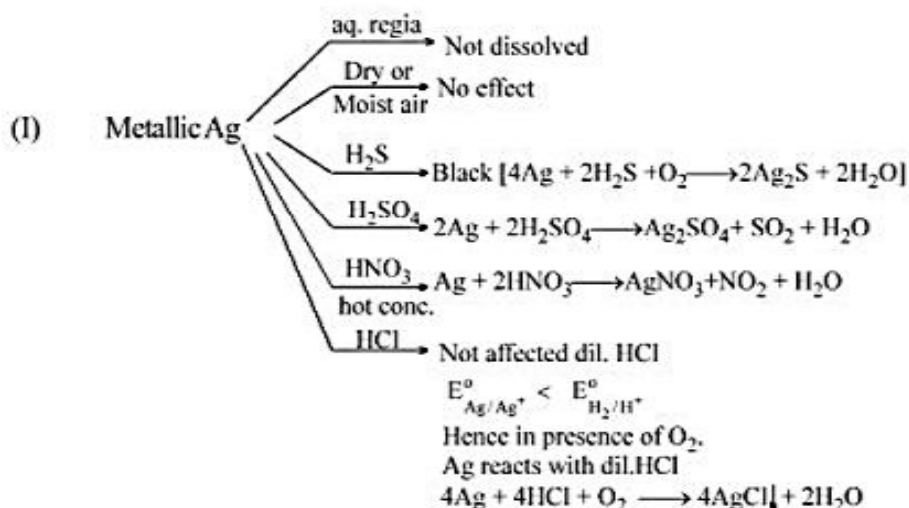
- (v) It oxidises nitrites to nitrates



- (vi) It oxidises oxalates or oxalic acid to carbon dioxide



## COMPOUNDS OF SILVER



In the same way in presence of  $O_2$ , Ag complexes with NaCN / KCN.  
 $4Ag + 8KCN + 2H_2O + O_2 \longrightarrow 4K[Ag(CN)_2] + 4KOH$

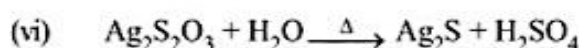
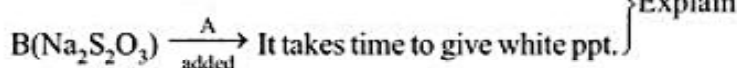
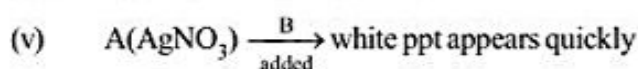
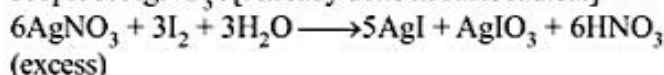
### $AgNO_3$

Prep<sup>n</sup>.: already done.

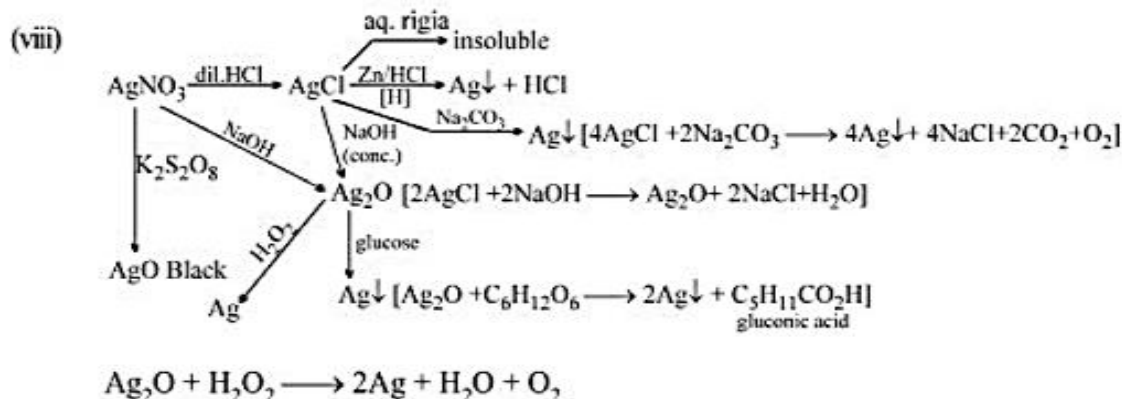
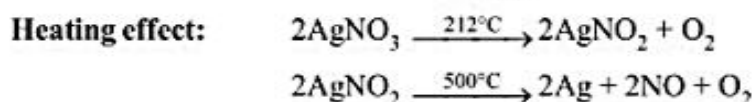
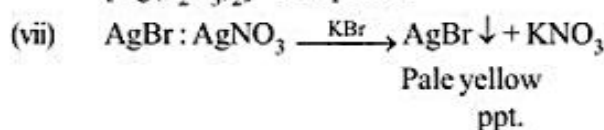
Properties.: (i) It is called as lunar caustic because in contact with skin it produces burning sensation like that of caustic soda with the formation of finely divided silver (black colour)

(ii) Thermal decomposition:

(iii) Props. of  $AgNO_3$  : [Already done in basic radical]

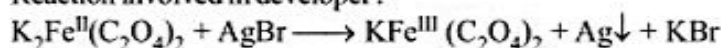


$AgCl$ ,  $AgBr$ ,  $AgI$  (but not  $Ag_2S$ ) are soluble in  $Na_2S_2O_3$  forming  $[Ag(S_2O_3)_2]^{-3}$  complexes



\*  $AgO$  supposed to be paramagnetic due to  $d^9$  configuration. But actually it is diamagnetic and exists as  $Ag^I [Ag^{III}O_2]$

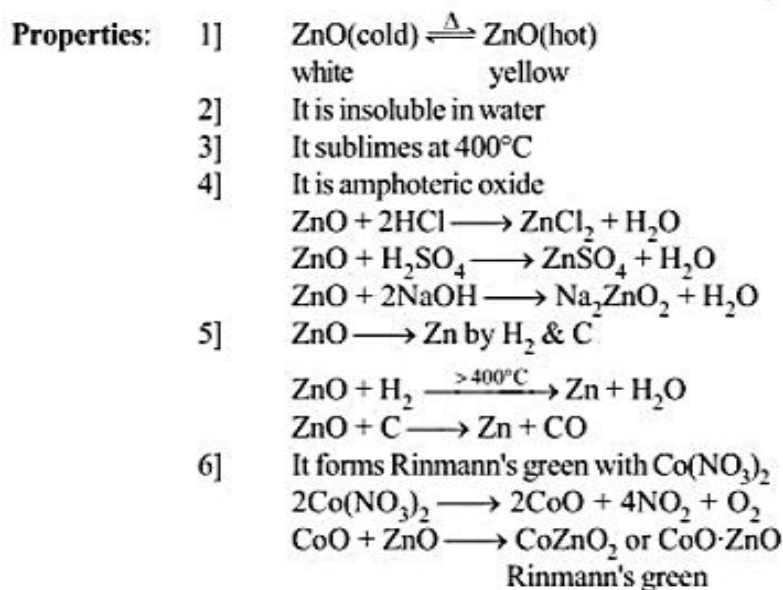
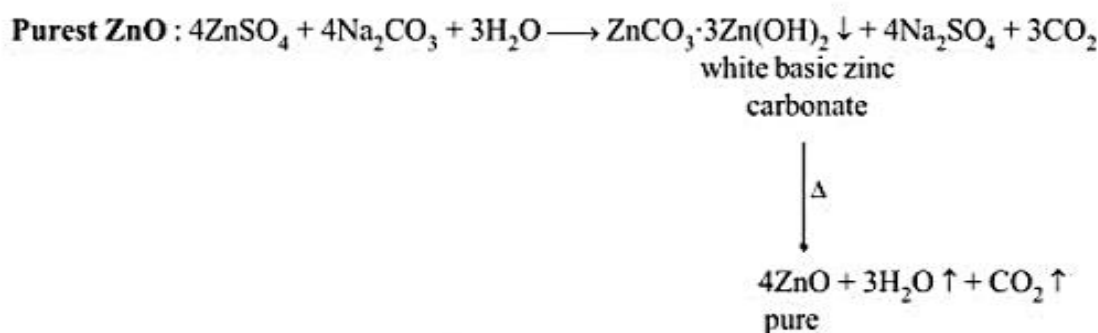
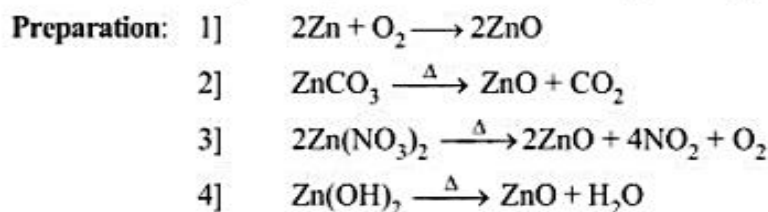
\* Reaction involved in developer :





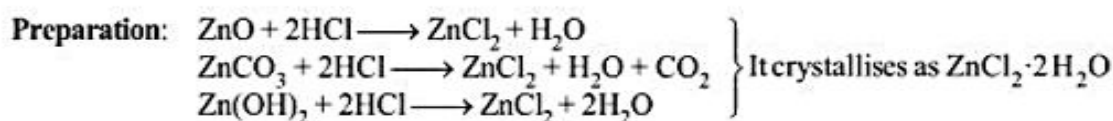
## COMPOUNDS OF ZINC

**ZnO:** It is called as phillospher's wool due to its wooly flock type appearance

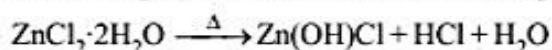


- Uses:**
- (1) As white pigment. It is superior than white lead because it does not turn into black
  - (2) Rinmann's green is used as green pigment
  - (3) It is used as zinc ointment in medicine

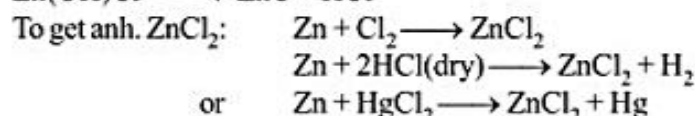
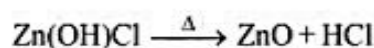
### ZnCl<sub>2</sub>



Anh.  $\text{ZnCl}_2$  cannot be made by heating  $\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$  because





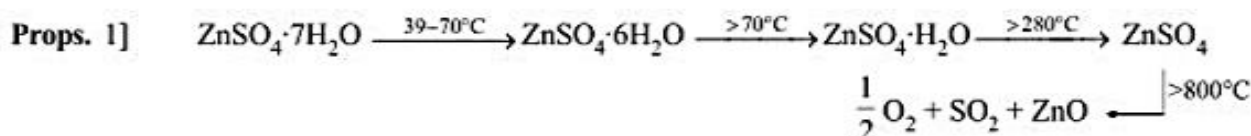
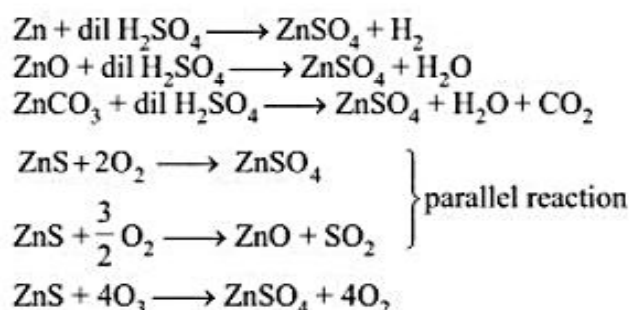


- Properties:**
- (i) It is deliquescent white solid (when anhydrous)
  - (ii)  $\text{ZnCl}_2 + \text{H}_2\text{S} \longrightarrow \text{ZnS}$
  - "  $+ \text{NaOH} \longrightarrow \text{Zn(OH)}_2 \xrightarrow{\text{excess}} \text{Na}_2[\text{Zn(OH)}_4]$
  - "  $+ \text{NH}_4\text{OH} \longrightarrow \text{Zn(OH)}_2 \xrightarrow{\text{excess}} [\text{Zn(NH}_3)_4]^{2+}$

- Uses:**
- 1] Used for impregnating timber to prevent destruction by insects
  - 2] As dehydrating agent when anhydrous
  - 3]  $\text{ZnO} \cdot \text{ZnCl}_2$  used in dental filling

### $\text{ZnSO}_4$ :

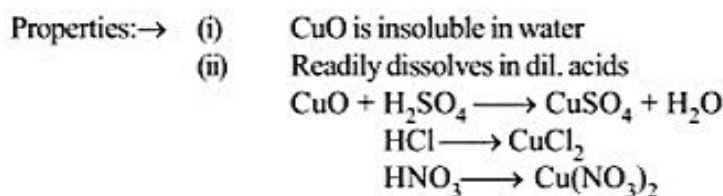
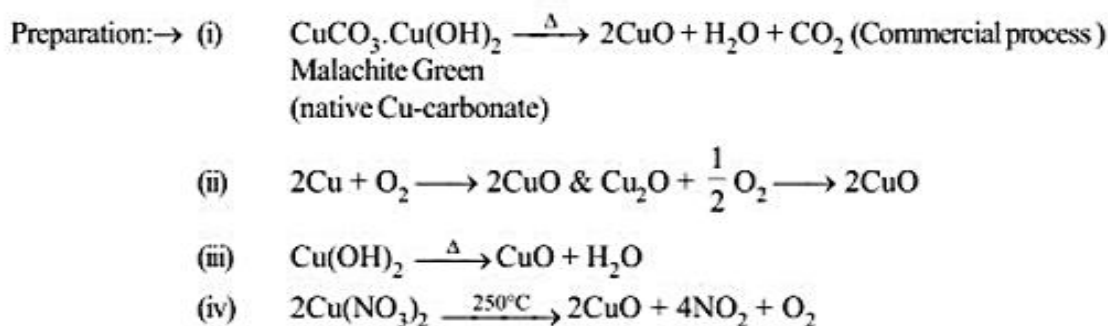
Preparation:  $\rightarrow$



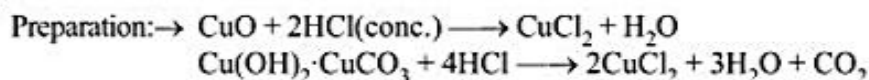
- Uses:**
- 1] in eye lotion
  - 2] Lithophone making ( $\text{ZnS} + \text{BaSO}_4$ ) as white pigment

## COMPOUNDS OF COPPER

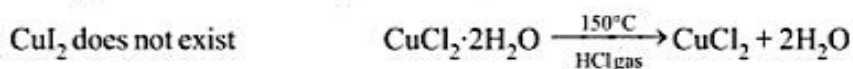
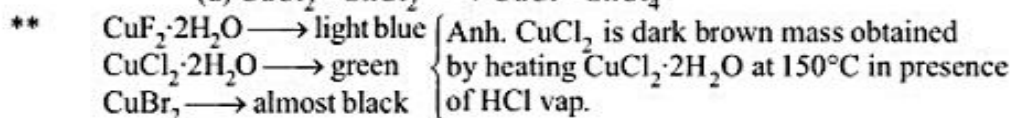
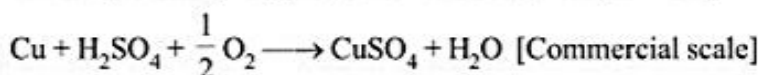
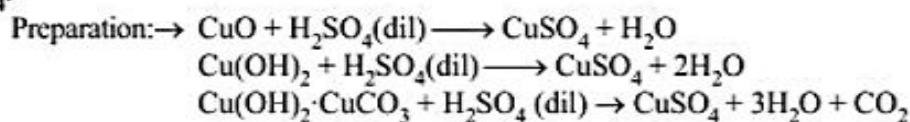
### $\text{CuO}$ :



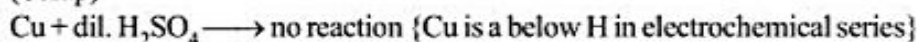
- (iii) It decomposes when, heated above  $1100^{\circ}\text{C}$   
 $4\text{CuO} \longrightarrow 2\text{Cu}_2\text{O} + \text{O}_2$
- (iv)  $\text{CuO}$  is reduced to  $\text{Cu}$  by  $\text{H}_2$  or  $\text{C}$  under hot condition  
 $\text{CuO} + \text{C} \longrightarrow \text{Cu} + \text{CO} \uparrow$   
 $\text{CuO} + \text{H}_2 \longrightarrow \text{Cu} + \text{H}_2\text{O} \uparrow$

 **$\text{CuCl}_2$ :**

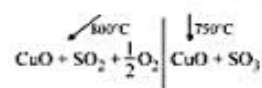
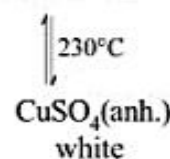
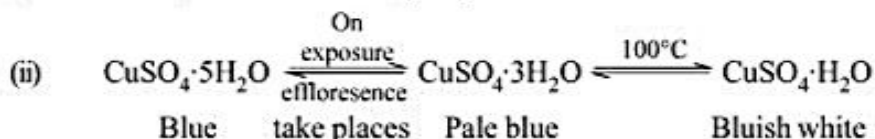
- Properties:  $\rightarrow$
- It is crystallised as  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  of Emerald green colour
  - dil. solution in water is blue in colour due to formation of  $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$  complex.
  - conc.  $\text{HCl}$  or  $\text{KCl}$  added to dil. solution of  $\text{CuCl}_2$  the colour changes into yellow, owing to the formation of  $[\text{CuCl}_4]^{2-}$
  - The conc. aq. solution is green in colour having the two complex ions in equilibrium  $2[\text{Cu}(\text{H}_2\text{O})_4]\text{Cl}_2 \rightleftharpoons [\text{Cu}(\text{H}_2\text{O})_4]^{2+} + [\text{CuCl}_4]^{2-} + 4\text{H}_2\text{O}$
  - $\text{CuCl}_2 \longrightarrow \text{CuCl}$  by no. of reagents
    - $\text{CuCl}_2 + \text{Cu-turnings} \xrightarrow{\Delta} 2\text{CuCl}$
    - $2\text{CuCl}_2 + \text{H}_2\text{SO}_3 + \text{H}_2\text{O} \longrightarrow 2\text{CuCl} + 2\text{HCl} + 2\text{H}_2\text{SO}_4$
    - $2\text{CuCl}_2 + \text{Zn}/\text{HCl} \longrightarrow 2\text{CuCl} + \text{ZnCl}_2$
    - $\text{CuCl}_2 + \text{SnCl}_2 \longrightarrow \text{CuCl} + \text{SnCl}_4$

 **$\text{CuSO}_4$ :**

(Scrap)



- Properties:  $\rightarrow$  (i) It is crystallised as  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$



- (iii) Revision with all others reagent

## COMPOUNDS OF IRON

### $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ :

- Preparation:→ (i)  $\text{Scrap Fe} + \text{H}_2\text{SO}_4 \xrightarrow{\text{(dil.)}} \text{FeSO}_4 + \text{H}_2\uparrow$
- (ii) From Kipp's waste  
 $\text{FeS} + \text{H}_2\text{SO}_4(\text{dil}) \longrightarrow \text{FeSO}_4 + \text{H}_2\text{S}\uparrow$
- (iii)  $\text{FeS}_2 + 2\text{H}_2\text{O} + \frac{7}{2}\text{O}_2 \longrightarrow \text{FeSO}_4 + \text{H}_2\text{SO}_4$
- Properties:→ (i) It undergoes aerial oxidation forming basic ferric sulphate  
 $4\text{FeSO}_4 + \text{H}_2\text{O} + \text{O}_2 \longrightarrow 4\text{Fe}(\text{OH})\text{SO}_4$
- (ii)  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O} \xrightarrow{300^\circ\text{C}} \text{FeSO}_4 \xrightarrow[\text{temp.}]{\text{high}} \text{Fe}_2\text{O}_3 + \text{SO}_2 + \text{SO}_3$   
 anh. white
- (iii) Aq. solution is acidic due to hydrolysis  
 $\text{FeSO}_4 + 2\text{H}_2\text{O} \rightleftharpoons \text{Fe}(\text{OH})_2 + \text{H}_2\text{SO}_4$   
 weak base
- (iv) It is a reducing agent  
 (a)  $\text{Fe}^{2+} + \text{MnO}_4^- + \text{H}^+ \longrightarrow \text{Fe}^{3+} + \text{Mn}^{2+} + \text{H}_2\text{O}$   
 (b)  $\text{Fe}^{2+} + \text{Cr}_2\text{O}_7^{2-} + \text{H}^+ \longrightarrow \text{Fe}^{3+} + \text{Cr}^{3+} + \text{H}_2\text{O}$   
 (c)  $\text{Au}^{3+} + \text{Fe}^{2+} \longrightarrow \text{Au} + \text{Fe}^{3+}$   
 (d)  $\text{Fe}^{2+} + \text{HgCl}_2 \longrightarrow \text{Hg}_2\text{Cl}_2\downarrow + \text{Fe}^{3+}$   
 white ppt.
- (v) It forms double salt. Example  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$

### $\text{FeO}$ (Black):

- Prep<sup>n</sup>:  $\text{FeC}_2\text{O}_4 \xrightarrow[\text{in absence of air}]{\Delta} \text{FeO} + \text{CO} + \text{CO}_2$
- Props:→ It is stable at high temperature and on cooling slowly disproportionates into  $\text{Fe}_3\text{O}_4$  and iron  
 $4\text{FeO} \longrightarrow \text{Fe}_3\text{O}_4 + \text{Fe}$

### $\text{FeCl}_2$ :

- Prep<sup>n</sup>:  $\text{Fe} + 2\text{HCl} \xrightarrow[\text{a current of HCl}]{\text{heated in}} \text{FeCl}_2 + \text{H}_2$   
 OR  
 $2\text{FeCl}_3 + \text{H}_2 \xrightarrow{\Delta} 2\text{FeCl}_2 + 2\text{HCl}$
- Props:→ (i) It is deliquescent in air like  $\text{FeCl}_3$
- (ii) It is soluble in water, alcohol and ether also because it is sufficiently covalent in nature
- (iii) It volatilises at about  $1000^\circ\text{C}$  and vapour density indicates the presence of  $\text{Fe}_2\text{Cl}_4$ . Above  $1300^\circ\text{C}$  density becomes normal
- (iv) It oxidises on heating in air  
 $12\text{FeCl}_2 + 3\text{O}_2 \longrightarrow 2\text{Fe}_2\text{O}_3 + 8\text{FeCl}_3$
- (v)  $\text{H}_2$  evolves on heating in steam  
 $3\text{FeCl}_2 + 4\text{H}_2\text{O} \longrightarrow \text{Fe}_3\text{O}_4 + 6\text{HCl} + \text{H}_2$
- (vi) It can exist as different hydrated form  
 $\text{FeCl}_2 \cdot 2\text{H}_2\text{O} \longrightarrow \text{colourless}$   
 $\text{FeCl}_2 \cdot 4\text{H}_2\text{O} \longrightarrow \text{pale green}$   
 $\text{FeCl}_2 \cdot 6\text{H}_2\text{O} \longrightarrow \text{green}$



$\text{FeCl}_3$ :	Prep <sup>n</sup> :	Anhydrous ferric chloride is prepared by heating metallic iron in a stream of dry chlorine gas.
	(i)	$\text{FeCl}_3$ solid is almost black. It sublimes at about $300^\circ\text{C}$ , giving a dimeric gas.
	(ii)	$\text{FeCl}_3$ dissolves in both ether and water, giving solvated monomeric species.
	(iii)	Iron (III) chloride is usually obtained as yellow-brown lumps of the hydrate $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ .
	(iv)	This is very soluble in water and is used both as an oxidizing agent, and as a mordant in dyeing.
	(v)	$\text{FeCl}_3$ is also used in the manufacture of $\text{CCl}_4$ .

### Illustration

**Q.1** The ions of d-block elements are mostly paramagnetic-

- (A) Because their d-orbitals are complete
- (B) Because they have mostly paired electrons
- (C) Because they have mostly unpaired electrons
- (D) Because they form coloured ions.

**Ans.** [C]

**Sol.** All atomic and molecular species which contains one or more unpaired electrons are paramagnetic. Most of the ions of transition elements have unpaired electrons. Hence they are all paramagnetic. Some ions of d-block elements with no unpaired electrons are  $\text{Sc}^{+3}$ ,  $\text{Ti}^{+4}$ ,  $\text{Zn}^{+2}$  and  $\text{Cu}^{+1}$ . These ions are not paramagnetic and they are also without colour.

**Q.2** Silver jewelry can be made to retain its silvery white appearance by-

- (A) Coating the silver with a film of oxide by dipping the silver in conc.  $\text{HNO}_3$
- (B) Coating with a film of the insoluble chloride by dipping the silver in conc.  $\text{HNO}_3$
- (C) Plating with Palladium
- (D) Plating with gold

**Ans.** [C]

**Sol.** Silver jewelry easily gets blackened when exposed to sulphur compounds. In order to prevent this blackening of silver jewelry, it is coated with Pd.

**Q.3** The order of stability of complexes of ion  $\text{Cu}^{+2}$ ,  $\text{Ni}^{+2}$ ,  $\text{Mn}^{+2}$  and  $\text{Fe}^{+2}$  decreases in the order-

- (A)  $\text{Cu}^{+2} > \text{Ni}^{+2} > \text{Fe}^{+2} > \text{Mn}^{+2}$
- (B)  $\text{Mn}^{+2} > \text{Ni}^{+2} > \text{Cu}^{+2} > \text{Fe}^{+2}$
- (C)  $\text{Ni}^{+2} > \text{Cu}^{+2} > \text{Fe}^{+2} > \text{Mn}^{+2}$
- (D)  $\text{Fe}^{+2} > \text{Ni}^{+2} > \text{Cu}^{+2} > \text{Mn}^{+2}$

**Ans.** [A]

**Sol.** The order of stability of the complexes of some of the ions carrying the same charge but differing in ionic radii decrease as the ionic radii increase.

ion	$\text{Cu}^{+2}$ ,	$\text{Ni}^{+2}$ ,	$\text{Fe}^{+2}$ ,	$\text{Mn}^{+2}$
Ionic radii	0.69	0.78	0.83	0.91

The complexes of  $\text{Cu}^{+2}$  are most stable while  $\text{Mn}^{+2}$  is least stable.



- Q.4 The elements which exhibit both vertical and horizontal similarities are –  
(A) Inert gas elements (B) Representative elements  
(C) Rare elements (D) Transition elements

Ans. [D]

Sol. It is a characteristic of transition elements. Vertical relationship is due to similar electronic configuration in a gp and horizontal relationship due to shielding effect being more predominant in last five elements in a period.

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### Exercise

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- Q.1 Transition metals and their oxides are used in industrial processes as –  
(A) Detergents (B) Insecticides (C) Catalysts (D) None

Ans. [C]

- Q.2 A blue solution of copper sulphate becomes darker when treated with excess of ammonia. This is because –  
(A) ammonia molecules replace water molecules in the solution  
(B) ammonia is stronger ligand than water  
(C) ammonia forms a stable complex ion  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  with  $\text{Cu}^{2+}$  ions  
(D) All are correct

Ans. [D]

- Q.3 A metal gives two chlorides 'A' and 'B'. 'A' gives black precipitate with  $\text{NH}_4\text{OH}$  and 'B' gives white. With KI 'B' gives a red precipitate, soluble in excess of KI. 'A' and 'B' are respectively –  
(A)  $\text{HgCl}_2$  and  $\text{Hg}_2\text{Cl}_2$  (B)  $\text{Hg}_2\text{Cl}_2$  and  $\text{HgCl}_2$  (C)  $\text{HgCl}_2$  and  $\text{HgCl}$  (D) None of these

Ans. [B]

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## f-Block Elements

They were earlier called as rare earth metals as it was believed that they exist in earth's crust to a very less extent for e.g. : Pm, does not exist in the earth's crust. But this terminology is now not applicable as they exist in earth's crust to a sufficient extent.

### (A) INNER TRANSITION ELEMENTS

The elements in which the additional electron enters in  $(n - 2)$  f orbitals are called inner **transition elements**, or **f-block elements**.

#### (a) Position in the periodic table

The lanthanides resemble yttrium in most of their properties. So it became necessary to accommodate all the fifteen elements together at one place. This has been done by placing the first element, lanthanum below yttrium and placing the remaining fourteen elements separately in the lower part of the periodic table.

Lanthanide series      ( $Z = 58 - 71$ )      (Ce – Lu)

Actinide series      ( $Z = 90 - 103$ )      (Th – Lw)

#### (b) Lanthanides (4f - block elements)

Lanthanides are reactive elements so do not found in free state in nature. Most important minerals for lighter Lanthanides are - Monazite, cerites and orthite and for heavier lanthanides - Gadolinite and Xenotime

#### (c) Electronic configuration

The general configuration of lanthanides may be given as  $4f^{2-14}5s^25p^65d^{0/1}6s^2$ . Lanthanides have outer three shells incomplete.

### Some properties of Lanthanoids

Element (pm)	Symbol	Atomic number	Outer configuration	Oxidation states	$M^{3+}$ radius
Lanthanum	La	57	[Xe] $5d^1, 6s^2$	+3	106
Cerium	Ce	58	[Xe] $4f^2, 6s^2$	+3, +4	103
Praseodymium	Pr	59	[Xe] $4f^3, 6s^2$	+3, +4	101
Neodymium	Nd	60	[Xe] $4f^4, 6s^2$	+2, +3, +4	100
Promethium	Pm	61	[Xe] $4f^5, 6s^2$	+3	98
Samarium	Sm	62	[Xe] $4f^6, 6s^2$	+2, +3	96
Europium	Eu	63	[Xe] $4f^7, 6s^2$	+2, +3	95
Gadolinium	Gd	64	[Xe] $4f^7, 5d^1, 6s^2$	+3	94
Terbium	Tb	65	[Xe] $4f^9, 6s^2$	+3, +4	92
Dysprosium	Dy	66	[Xe] $4f^{10}, 6s^2$	+3, +4	91
Holmium	Ho	67	[Xe] $4f^{11}, 6s^2$	+3	89
Erbium	Er	68	[Xe] $4f^{12}, 6s^2$	+3	88
Thulium	Tm	69	[Xe] $4f^{13}, 6s^2$	+2, +3	87
Ytterbium	Yb	70	[Xe] $4f^{14}, 6s^2$	+2, +3	86
Lutetium	Lu	71	[Xe] $4f^{14}, 5d^1, 6s^2$	+3	85

- (i) It is to be noted here that filling of 4f orbitals in the atoms is not regular. A 5d electron appears in gadolinium ( $z = 64$ ) with an outer electronic configuration of  $4f^7 5d^1 6s^2$  (and not  $4f^8 6s^2$ ). This is because the 4f and 5d electrons are at about the same potential energy and that the atoms have a tendency to retain stable half filled configuration.
- (ii) On the other hand, the filling of f orbitals is regular in tripositive ions.
- (iii) After losing outer electrons, the f orbitals shrink in size and became more stable. Pm is the only synthetic radioactive lanthanide.

**(d) Oxidation states**

Lanthanides	Ce <sub>58</sub>	Pr <sub>59</sub>	Nd <sub>60</sub>	Pm <sub>61</sub>	Sm <sub>62</sub>	Eu <sub>63</sub>	Gd <sub>64</sub>	Tb <sub>65</sub>	Dy <sub>66</sub>	Ho <sub>67</sub>	Er <sub>68</sub>	Tm <sub>69</sub>	Yb <sub>70</sub>	Lu <sub>71</sub>
Oxidation	+3	+3	+3	+3	(+2)	+2	+3	+3	+3	+3	(+2)	(+2)	+2	+3
States	+4	(+4)			+3	+3		+4	(+4)		+3	+3	+3	

- (i) Oxidation states in brackets are unstable states
- (ii) The lanthanides contains two s electrons in the outermost shell, they are therefore expected to exhibit a characteristic oxidation state of +2. But for the lanthanides, the +3 oxidation is common.
- (iii) This corresponds to the use of two outermost electrons ( $6s^2$ ) alongwith one inner electron. The inner electron used is a 5d electron (in La, Gd and Lu), or one of the 4f electron if no 5d electrons present.
- (iv) All the lanthanides attains +3 oxidation state and only cerium, Praseodymium, and terbium exhibit higher oxidation state (+4).

Oxidation states + 2 and +4 occur particularly when they lead to

- (i) A noble gas configuration e.g.  $Ce^{4+}$  ( $f^0$ )
- (ii) A half filled 'f' orbital e.g.  $Eu^{2+}$ ,  $Tb^{4+}$ , ( $f^7$ )
- (iii) A completely filled 'f' orbital e.g.  $Yb^{2+}$  ( $f^{14}$ )

Therefore, in higher oxidation state, they act as oxidising while in lower state as reducing agents.

**(e) Magnetic properties**

In tripositive lanthanide ions the number of unpaired electrons regularly increases from lanthanum to Gadolinium (0 to 7) and then continuously decreases upto lutecium (7 to 0). So lanthanum and lutecium ions which are diamagnetic, all other tripositive lanthanide ions are Paramagnetic.

**Colour** - The lanthanide ions have unpaired electrons in their 4f orbitals. Thus these ions absorb visible region of light and undergo f-f transition and hence exhibit colour. The colour exhibited depends on the number of unpaired electrons in the 4f orbitals. The ions often with  $4f^n$  configuration have similar colour to those ions having  $4f^{14-n}$  configuration.

Lanthanide ions having  $4f^0$ ,  $4f^7$ ,  $4f^{14}$  are colourless. Lanthanide ions  $4f^1$  and  $4d^{13}$  are also colourless.

**(f) Other Properties :**

- (a) Highly dense metals with high m.pt. (do not show any regular trend).
- (b) **Ionisation Energies** - Lanthanides have fairly low ionisation energies comparable to alkaline earth metals.
- (c) **Electro positive Character** - High due to low I.P.
- (d) **Complex formation** - Do not have much tendency to form complexes due to low charge density because of their large size.  
 $Lu^{+3}$  is smallest in size can only form complex.



- (e) **Reducing Agent** - They readily lose electrons so are good reducing agent.
- In +3 oxidation states, nitrates, perchlorates and sulphates of lanthanides and actinides are water soluble, while their hydroxides, fluorides and carbonates are water insoluble.
  - Alloys of lanthanides with Fe are called misch metals.
  - $\text{La}(\text{OH})_3$  is most basic in nature while  $\text{Lu}(\text{OH})_3$  least basic.
  - Lanthanides form  $\text{MC}_2$  type carbide with carbon, which on hydrolysis gives  $\text{C}_2\text{H}_2$ .

## (B) LANTHANIDE CONTRACTION

- In the lanthanide series with increasing atomic number, there is a progressive decrease in the size from lanthanum to lutetium or from  $\text{La}^{+3}$  to  $\text{Lu}^{+3}$ . This contraction in size is known as lanthanide contraction.
- The general electronic configuration of these elements is  $4f^{0-14}5s^2p^6d^{0-1}6s^2$ . In these elements the added electron enters the deep seated f-orbitals and therefore experiences considerable pull by the nucleus.
- Such an electron cannot add to the size of the element and also because the intervening  $5s^2p^6d^1$  electronic shells, it is very little screening effect on the outermost  $6s^2$  electrons. Hence with increasing atomic number, the enhanced nuclear charge leads to contraction in the size of atoms and ions.
- The atomic volumes of europium and ytterbium are unexceptedly large. The large atomic size of Eu and Yb suggest weaker bonding in the solid elements. Both these elements have only two electrons extra than the stable configurations (half filled,  $f^7$ , and completely filled,  $f^{14}$ ), hence they utilise two electrons in metallic bonding as in the case with barium.

## (C) EFFECTS OF LANTHANIDE CONTRACTION

- Close resemblace of Lanthanides :-** The general decrease in the sizes of the lanthanides with an increase in their nuclear charges result in a small increase in their ionisation energies. Hence their basic and ionic nature gradually decreases from La to Lu. This also explains the variations in properties such as increased tendency for hydrolysis and formation of complex salts and decreased thermal stability. solubility of their salts.
- Similarity of yttrium with lanthanides :-** The properties of yttrium are so similar to the lanthanides that it is considered more a member of the lanthanide series than a congener of scandium.
- Anomalous behaviour of post-lanthanides :-** The following anomalies may be observed in the behaviour of post-lanthanide elements.
  - Atomic size** - The ionic radii of  $\text{Zr}^{+4}$  is about 9% more than  $\text{Ti}^{+4}$ . Similar trend is not maintained on passing from the second to third transition series. The ionic radius of  $\text{Hf}^{+4}$ , instead of increasing (because of inclusion of one more electronic shell). decreases (or is virtually equal to  $\text{Zr}^{+4}$ ) as a consequence of the lanthanide contraction. This explains the close similarities between the members of the second and third transition series than between the elements of the first and second series.
  - Ionisation potential and electronegativity :-** The effect of lanthanide contraction is also seen in the increase in the ionisation potential values and electronegativities of the elements of the third transition series, contrary to the general trend.



Because of the lanthanide contraction, the post-lanthanide elements have stronger positive field and thus the electrons are held more tightly.

The greater effective nuclear charge of the former make them more electronegative than the latter.

(c) **High density** :- Because of lanthanide contraction the atomic sizes of the post lanthanide elements become very small. consequently, the packing of atoms in their metallic crystals become so much compact that their densities are very high.

The densities of the third transition series elements are almost double to those of the second series elements.

## (D) APPLICATION OF LANTHANIDES

Cerium is most useful element in the lanthanides

- Ceramic application -  $\text{CeO}_2$ ,  $\text{La}_2\text{O}_3$ ,  $\text{Nd}_2\text{O}_3$  and  $\text{Pr}_2\text{P}_3$  are used as decolourizing agents for glasses.
- $\text{CeS}$  (m.p. -  $2000^\circ\text{C}$ ) is used in the manufacture of a special type of crucibles and refractories.
- Lanthanide compounds like cerium molybdate, cerium tungstate are used as paints and dyes.
- In textile and leather industries (Ce salts).

## (E) ACTINIDES (5f - BLOCK ELEMENTS)

- The elements in which the extra electron enters 5f-orbitals of (n - 2)th main shell are known as actinides.
- The man-made eleven elements  $\text{Np}_{93}$  -  $\text{Lr}_{103}$  are placed beyond uranium in the periodic table and are collectively called trans-uranic elements.
- Th, Pa and U first three actinides are natural elements.

(a) **Electronic configuration** :-

The general configuration of actinides may be given as  $5f^{1-14} 6d^{0/1} 7s^2$ .

Some properties of actinoids				
Element	Symbol	Atomic number	Configuration	Oxidation states
Actinium	Ac	89	$[\text{Rn}] 6d^1, 7s^2$	+3
Thorium	Th	90	$[\text{Rn}] 6d^2, 7s^2$	+3, +4
Protactinium	Pa	91	$[\text{Rn}] 5f^2, 6d^1, 7s^2$	+3, +4, +5
Uranium	U	92	$[\text{Rn}] 5f^3, 6d^1, 7s^2$	+3, +4, +5, +6
Neptunium	Np	93	$[\text{Rn}] 5f^4, 6d^1, 7s^2$	+3, +4, +5, +6, +7
Plutonium	Pu	94	$[\text{Rn}] 5f^6, 7s^2$	+3, +4, +5, +6, +7
Americium	Am	95	$[\text{Rn}] 5f^7, 7s^2$	+2, +3, +4, +5, +6
Curium	Cm	96	$[\text{Rn}] 5f^7, 6d^1, 7s^2$	+3, +4
Berkelium	Bk	97	$[\text{Rn}] 5f^8, 6d^1, 7s^2$	+3, +4
Californium	Cf	98	$[\text{Rn}] 5f^{10}, 7s^2$	+2, +3
Einsteinium	Es	99	$[\text{Rn}] 5f^{11}, 7s^2$	+2, +3
Fermium	Fm	100	$[\text{Rn}] 5f^{12}, 7s^2$	+2, +3
Mendelevium	Md	101	$[\text{Rn}] 5f^{13}, 7s^2$	+2, +3
Nobelium	No	102	$[\text{Rn}] 5f^{14}, 7s^2$	+2, +3
Lawrencium	Lr	103	$[\text{Rn}] 5f^{14}, 6d^1, 7s^2$	+3

## SOLVED EXAMPLES

- Q.1** Which of the following statements is correct?  
 (A) Iron belongs to third transition series of the periodic table  
 (B) Iron belongs to f-block of the periodic table  
 (C) Iron belongs to first transition series  
 (D) Iron belongs to group VIII of the periodic table

**Ans.** [C]

**Sol.** The correct statement is that iron belongs to first transition series of elements. It is called 3d series. The members of this series are

Sc Ti V Cr Mn Fe Co Ni Cu Zn

The electronic config. of  $\text{Fe}^{2+}$  is  $3d^6, 4s^2$

- Q.2** Zn and Hg do not show variable valency like d-block elements because-

- (A) They are soft  
 (B) Their d-shells are complete  
 (C) They have only two electrons in the outermost subshell  
 (D) Their d-shells are incomplete

**Ans.** [B]

**Sol.** Zn and Hg do not show variable valency like d-block elements because their d-shell are complete their electronic config. are

$\text{Zn}^{30} \quad 3d^{10}, 4s^2$

$\text{Hg}^{48} \quad 4d^{10}, 5s^2$

The variable valency is shown by those elements which have got incompletely filled d-orbitals

- Q.3** A metal ion from the first transition series has a magnetic moment (calculated) of 2.83 BM. How many unpaired electrons are expected to be present in the ion?

- (A) 1 (B) 2 (C) 3 (D) 4

**Ans.** [B]

**Sol.** A metal ion from the first transition series has a magnetic moment (calculated) of 2.83 BM. The no. of unpaired electrons are expected to be present in the ion are 2

$$\mu = \sqrt{n(n+2)} = \sqrt{2(2+2)}$$

$$= 2 \cdot \sqrt{2} = 2 \times 1.414 = 2.828 \text{ B.M} = 2.83 \text{ B.M}$$

- Q.4** Out of the compounds  $\text{K}_2\text{SO}_4$ ,  $\text{MgCl}_2$ ,  $\text{FeSO}_4$ ,  $\text{NiCl}_2$  and  $\text{ZnO}$  which of the following pair will show paramagnetism-

- (A)  $\text{K}_2\text{SO}_4$ ,  $\text{MgCl}_2$  (B)  $\text{ZnO}$ ,  $\text{MgCl}_2$  (C)  $\text{K}_2\text{SO}_4$ ,  $\text{ZnCl}_2$  (D)  $\text{FeSO}_4$ ,  $\text{NiCl}_2$

**Ans.** [D]

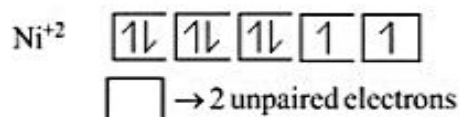
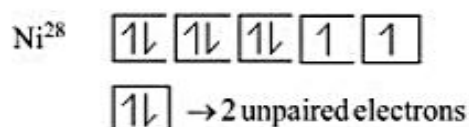
**Sol.** The pair which shows paramagnetism is  $\text{FeSO}_4$  and  $\text{NiCl}_2$ . It consist of  $\text{Fe}^{+2}$  and  $\text{Ni}^{+2}$  ions which have got unpaired electrons. Their electronic configs. are as given below.

$\text{Fe}^{26} \quad \boxed{1\downarrow} \boxed{1} \boxed{1} \boxed{1} \boxed{1}$

$\boxed{1\downarrow} \rightarrow 4 \text{ unpaired electrons}$

$\text{Fe}^{+2} \quad \boxed{1\downarrow} \boxed{1} \boxed{1} \boxed{1} \boxed{1}$

$\boxed{\phantom{1\downarrow}} \rightarrow 4 \text{ unpaired electrons}$



**Q.5** Variable valency is generally shown by-

- (A) s-block elements  
 (B) p-block elements  
 (C) Transition elements  
 (D) All elements in periodic table

**Ans.** [C]

**Sol.** One of the most striking features of the transition elements, is that they exhibit variable valency. The variable valency occurs to some extent in the p-block elements also. In this case the valency changes usually in units of two. Some example are  $\text{SnCl}_2$ ,  $\text{SnCl}_4$ ,  $\text{PCl}_3$ ,  $\text{PCl}_5$  etc. But in transition elements the valency changes in one unit e.g  $\text{Cu}^+$ ,  $\text{Cu}^{+2}$ ,  $\text{Fe}^{+2}$ ,  $\text{Fe}^{+3}$  etc.

**Q.6** The common oxidation states of gold are-

- (A) 1, 2 and 3                      (B) 1, 3                      (C) 2 and 3                      (D) 3, 4

**Ans.** [B]

**Sol.** The common oxidation states of gold are +1 and +3. The +3 state is more stable. This is explained on the basis that +1 ion gets disproportionate.



**Q.7** The d-block elements easily form alloys because-

- (A) Their d-block are only partly filled  
 (B) They have very widely differing atomic sizes.  
 (C) They are very similar in their atomic sizes  
 (D) They are highly electronegative in character

**Ans.** [C]

**Sol.** In the case of the transition metals the atomic radii have values which are very close, that is they are of very similar size. Hence the atom of an element in a crystal lattice can easily be replaced by a metal atom of another transition elements. This makes metals form alloys very easily.

**Q.8** Wilkinson's catalyst used as a homogenous catalyst in the hydrogenation of alkene contains-

- (A) Fe                      (B) Al                      (C) Rh                      (D) Co

**Ans.** [C]

**Sol.** Wilkinson's catalyst contains Rh. The formula is  $(\text{Ph}_3\text{P})_3\text{RhCl}$ . It is used as homogeneous catalyst in the hydrogenation of alkenes.

**Q.9** Which of the following is the softest metals-

- (A) Sc                      (B) Zn                      (C) Ti                      (D) V

**Ans.** [B]

**Sol.** The softest metal is Zn, while remaining all other metal are comparatively harder metals.



**Q.10** In which of the following transition metal ions d-d transition is possible-

- (A)  $\text{Cu}^+$  (B)  $\text{Zn}^{+2}$  (C)  $\text{Ti}^{+3}$  (D)  $\text{Sc}^{+3}$

**Ans.** [C]

**Sol.** The d-d transition is possible in  $\text{Ti}^{+3}$  because it has got  $3d^1$  configuration, hence one electron can easily go from one orbital to another in degenerate levels.

**Q.11** Which of the following cuprous compounds is not stable-

- (A)  $\text{CuCl}_2$  (B)  $\text{Cu}_2(\text{CNS})_2$  (C)  $\text{Cu}_2\text{Cl}_2$  (D)  $\text{Cu}_2\text{SO}_4$

**Ans.** [D]

**Sol.** The compound  $\text{Cu}_2\text{SO}_4$  is not stable because Cu is stabilized only in  $\text{Cu}^{+2}$  state in its compounds with  $\text{SO}_4^{-2}$  ions hence  $\text{Cu}_2\text{SO}_4$  is not stable while  $\text{CuSO}_4$  is stable.

**Q.12** A developer used in photography is—

- (A) A weak acid (B) A weak base  
(C) A mild reducing agent (D) An oxidizing agent

**Ans.** [C]

**Sol.** A developer is a weak reducing agent, e.g., Ferrous oxalate; the parts affected by light on photographic plate are reduced to the maximum extent whereas part not affected by light remains unaffected.



## SOLID STATE

### SOLIDS

Solids are characterised by the state of matter in which particles are closely packed and held together by strong inter molecular attractive force.

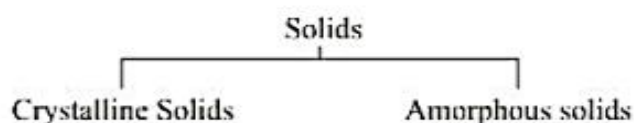
#### *Properties of solids*

- (a) In solid state the particles are not able to move randomly.
- (b) They have definite shape and volume.
- (c) Solids have high density.
- (d) Solids have high and sharp melting point which depends on the strength or value of binding energy.
- (e) They are very low compressible.
- (f) They show very slow diffusion.

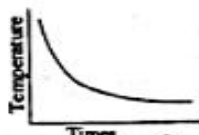
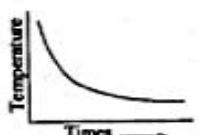


Can you guess which type of kinetic energy will be more dominant in solids, Rotational, translational or vibrational?

#### Types of Solids



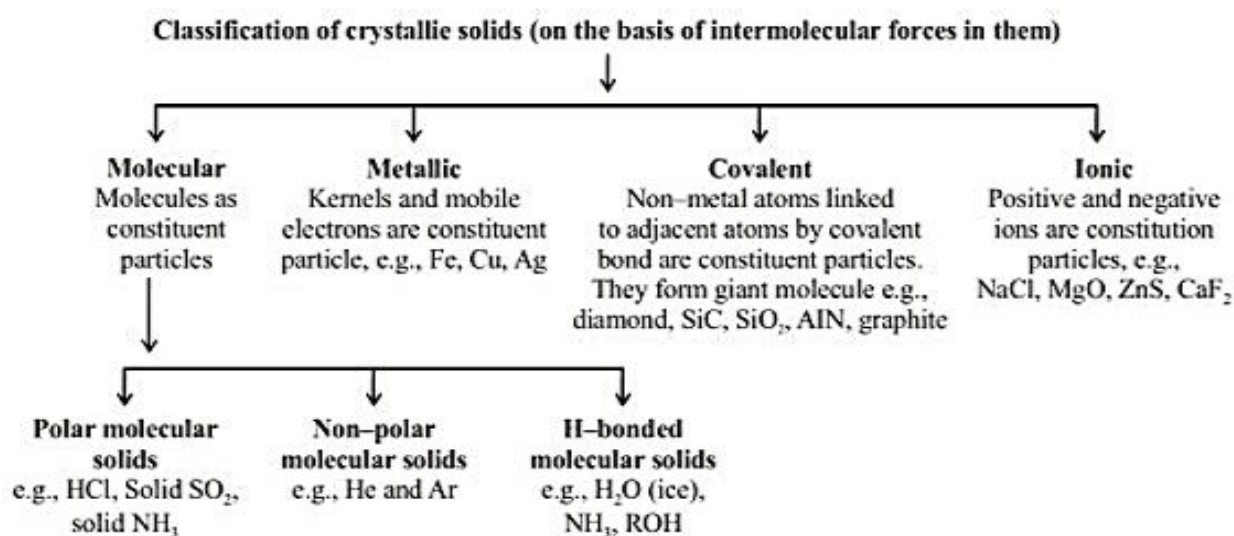
#### Difference between crystalline and amorphous solids

S.N.	Property	Crystalline solids	Amorphous solids
1	Shape	They have definite and regular geometrical form.	They do not have definite and regular geometrical form.
2	Melting point	They have definite melting point.	They do not have definite melting point.
3	Heat of fusion	They have a definite heat of fusion.	They do not have definite heat of fusion
4	Compressibility	They are rigid and incompressible.	These may be compressed to any appreciable extent.
5	Cutting with a Sharp edged tool	They give clean cleavage i.e. they break into two pieces with plane surfaces. 	They give irregular cleavage i.e. they break into two pieces with irregular surface. 
6	Isotropy and Anisotropy	They are anisotropic.	They are isotropic.
7	Physical state	True solids	pseudo solids and are considered as super cooled liquid.
	Examples	Quartz, Diamond	Rubber, Plastic

## CLASSIFICATION OF CRYSTALS

According to attractive force which hold crystal together are generally of five types and thus crystal can be classified into four types:

Type of Solid	Intermolecular forces	Properties	Examples
Ionic	Ion-Ion forces	Brittle, hard, high Melting point Insulator in solid but conductance fused and aqueous solution	NaCl, KCl, $\text{MgCl}_2$
Molecular	Dispersion forces/Dipole-Dipole /H-bond	Soft, low melting point, Insulators	$\text{H}_2\text{O}$ , $\text{Br}_2$ , $\text{CO}_2$ , $\text{CH}_4$
Covalent or network	Covalent bonds	Hard, Very high melting point	C-Diamond, $\text{SiO}_2$
Metallic	Metallic bonds	Variable hardness and melting point, malleable and ductile, conducting	Na, Zn, Cu, Fe



It is advisable that students should memories one or two examples of each type of crystalline solids.

### Type of Symmetry in Crystals

- a. **Law of symmetry** : It states that all crystals of a substance possess the same element of symmetry. Three important elements of symmetry are :
- I. Plane of symmetry      II. Axis of symmetry      III. Center of symmetry



b. The total number of elements of a symmetry in a cubic crystal = 23

I. Plane of symmetry = 3 (rectangular plane of symmetry)  
+ 6 (diagonal plane of symmetry) = 9

II. Axis of symmetry = 3 (four-fold or a tetrad axis of symmetry)  
+ 4 (three-fold or a triad axis of symmetry)  
+ 6 (two-fold or diad axis of symmetry) = 13

III. Center of symmetry or inversion of symmetry = 1

$\therefore$  Total number of elements of symmetry in a cubic crystals =  $9 + 13 + 1 = 23$



**Axis of six-fold or a hexed axis of symmetry :** This type of symmetry is possible in hexagonal crystals and not in cubic crystals.

## STUDY OF CYRSTALS

**Crystal** - A crystal is a homogenous portion of a solid substance made by regular pattern of structural units bonded by plane surface making definite angles with each other.

**Space lattice** - The arrangement of constituents like atom, ions and molecules in different sites in three dimensional space is called space lattice.

**Unit cell** - The smallest repeating unit in space lattice which when repeats over and over again, results in a crystal of the given substance called unit cell.

**Face** - The plane surface of the crystal are called faces.

**Edge** - An edge is formed by the intersection of two adjacent faces.

**Interfacial angle** - The angle between two perpendicular intersecting faces is called interfacial angles.

## CRYSTAL SYSTEM

Bravais showed that there are only seven types of crystal system.

These are -

- |                  |                  |
|------------------|------------------|
| (a) Cubic        | (b) Tetragonal   |
| (c) Orthorhombic | (d) Rhombohedral |
| (e) Hexagonal    | (f) Monoclinic   |
| (g) Triclinic    |                  |

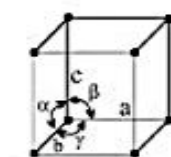


	Crystal Systems	Bravais Lattice	Unit Cell Parameters		Example
			Intercepts	Crystal Angles	
1	Cubic	Primitive, Face Centered, Body Centered	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	NaCl, Zinc blend, Cu
2	Orthorhombic	Primitive, Face Centered, Body Centered, End Centered	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	Rhombic sulphur, $\text{KNO}_3$ , $\text{BaSO}_4$
3	Tetragonal	Primitive, Body Centered	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	White tin, $\text{SnO}_2$ , $\text{TiO}_2$ , $\text{CaSO}_4$
4	Monoclinic	Primitive, End Centered	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ, \beta \neq 90^\circ$	Monoclinic sulphur, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$
5	Rhombohedral or Trigonal	Primitive	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	Calcite ( $\text{CaCO}_3$ ), HgS (Cinnabar)
6	Triclinic	Primitive	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	$\text{K}_2\text{Cr}_2\text{O}_7$ , $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , $\text{H}_3\text{BO}_3$
7	Hexagonal	Primitive	$a = b \neq c$	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$	Graphite, ZnO, CdS

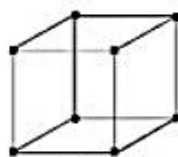


Students should memories all the cell parameters for each type of crystal systems. Remembering examples for each type is not required except for very common substances like NaCl, Graphite etc.

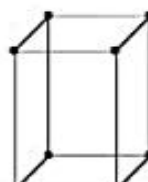
## SEVEN CRYSTAL SYSTEM



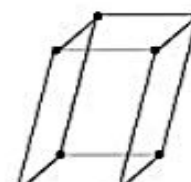
Simple Cubic  
 $a = b = c$   
 $\alpha = \beta = \gamma = 90^\circ$



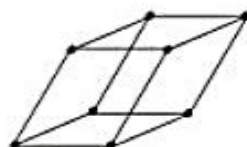
Orthorhombic  
 $a \neq b \neq c$   
 $\alpha = \beta = \gamma = 90^\circ$



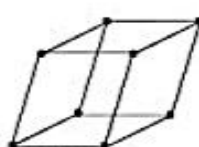
Tetragonal  
 $a = b \neq c$   
 $\alpha = \beta = \gamma = 90^\circ$



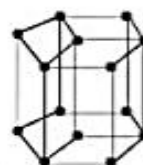
Monoclinic  
 $a \neq b \neq c$   
 $\alpha = \gamma = 90^\circ, \beta \neq 90^\circ$



Rhombohedral  
 $a = b = c$   
 $\alpha = \beta = \gamma \neq 90^\circ$



Triclinic  
 $a \neq b \neq c$   
 $\alpha \neq \beta \neq \gamma \neq 90^\circ$

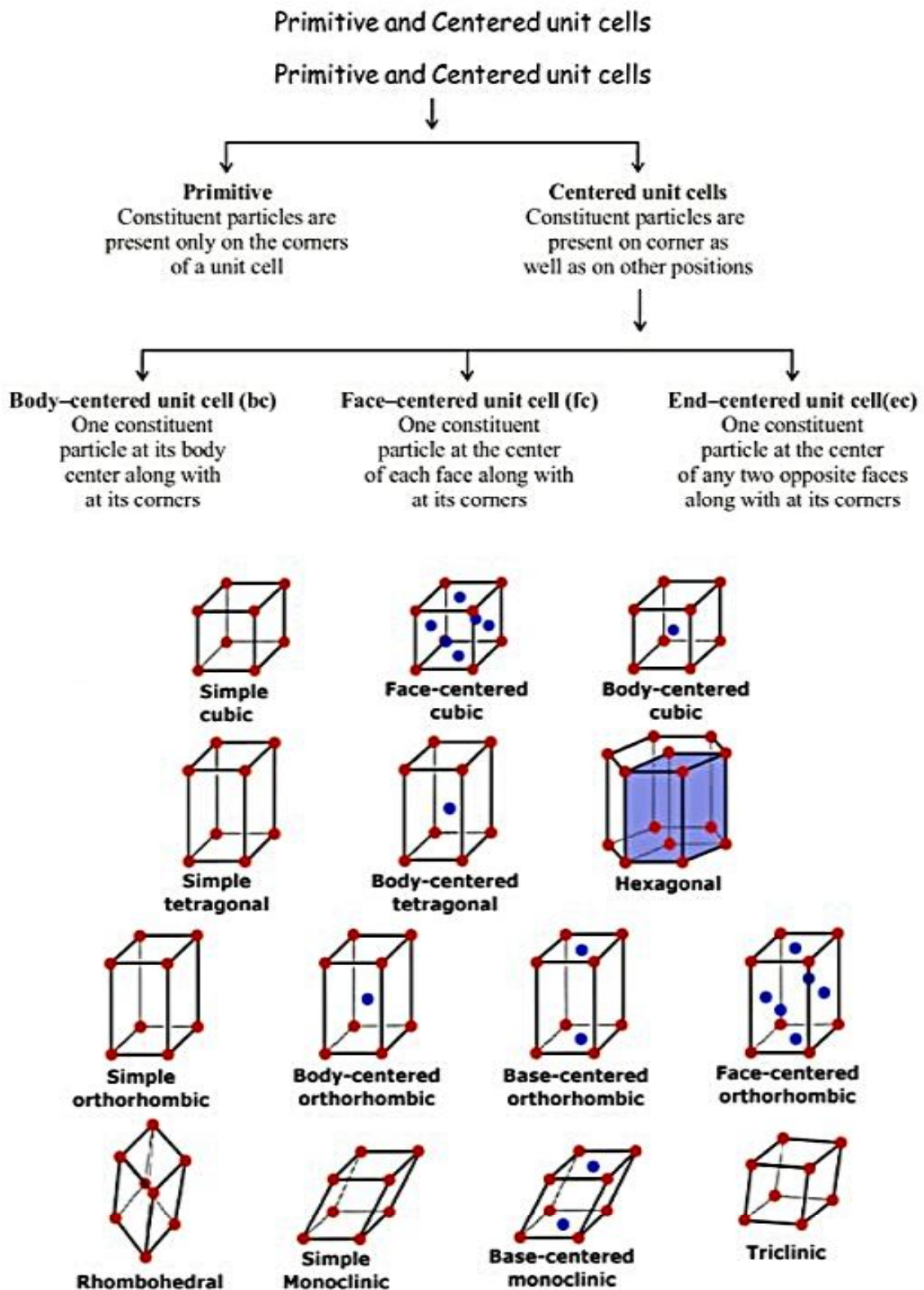


Hexagonal Primitive  
 $a = b \neq c$   
 $\alpha = \beta = 90^\circ, \gamma = 120^\circ$



Although there are only 7 crystal systems or shapes, there are 14 different crystal lattices, called Bravais Lattices. (3 different cubic types, 2 different tetragonal types, 4 different orthorhombic types, 2 different monoclinic types, 1 rhombohedral, 1 hexagonal, 1 triclinic).





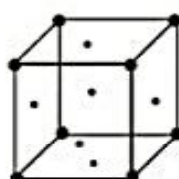
## TYPES OF UNIT CELLS

There are four types of unit cells (among the cubic system).

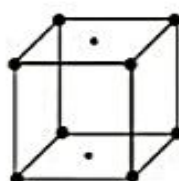
- (a) Simple or primitive. Particles are only at the corners of the unit cell.



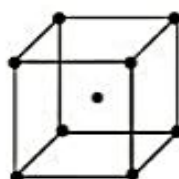
- (b) Face-centered cubic unit cell. In addition to corners, particles are present at the centre of each face of the unit cell.



- (c) End-face-centered cubic unit cell. A particle is present at each corner plus particles are present on the end faces of the unit cell.



- (d) Body-centered cubic unit cell. In addition to the particles at the corners, there is one particle in the body-centre of the unit cell.



### Coordination Number

If atoms are represented by spheres, the number of spheres which are touching a particular sphere is called *coordination number* of that sphere. In ionic crystals, the coordination number may be defined as the number of the oppositely charged ions surrounding a particular ion.

### The number of particles per Unit Cell

- (a) An atom at the corner is shared by 8 unit cells. Therefore, its contribution is  $= 1/8$ .  
 (b) An atom at the face is shared by 2 unit cells. Therefore, its contribution is  $= 1/2$ .  
 (c) An atom present in the body is unshared. Therefore, its contribution is 1.  
 (d) An atom present on the edge is shared by four unit cells. Therefore, its contribution is  $= 1/4$ .

Thus, in

- (e) a primitive or simple cubic unit cell, the total number of particles is  $1/8 \times 8 = 1$ .  
 (f) a face-centred cubic unit cell, the total number of particles is  $1/8 \times 8 + 1/2 \times 6 = 4$ .  
 (g) a body-centred cubic unit cell, the total number of particles is  $1/8 \times 8 + 1 = 2$ .

The number of atoms per unit cell are in the same ratio as the stoichiometry of the compound or the ratio of the number of particles A and B present per unit cell gives the formula of the compound formed between A and B

### Illustration

1. A compound formed by elements X and Y crystallises in the cubic structure, where Y atoms are at the corners of the cube and X atoms are at the alternate faces. What is the formula of the compound?

**Sol.** Y atoms are at the corners of the cubic unit cell and contribution of each is  $= 1/8$ . So, the total number of Y atoms per unit cell  $= 8 \times 1/8 = 1$ . X atoms are on alternate faces and contribution of each  $= 1/2$ . So, the number of X atoms per unit cell is  $2 \times 1/2 = 1$ . Hence, the formula is XY.

2. Calculate the number of atoms in a cubic unit cell having one atom on each corner and two atoms on each body diagonal.

**Sol.** Atoms at the corner contribute  $1/8$  and so the total number of corner atoms per unit cell is equal to one. Now, there would be four body diagonals in a cube and each diagonal has 2 atoms not shared by any other unit cell. So, there are total 8 atoms within the body of the unit cell and the total number of atoms per unit cell would be nine.

### Exercise

1. In a solid 'AB' having NaCl structure atoms, occupy the corners of the unit cell. If all the face centred atoms along one of the axis are removed, then the resultant stoichiometry of the solid is-

(A)  $AB_2$                       (B)  $A_2B$                       (C)  $A_4B_3$                       (D)  $A_3B_4$

**Ans.** (C)

### Packing of Constituent Particles in Crystals

The structure of crystalline solids is determined by the packing of their constituents. During formation, the constituent particles get closely packed together. The available space is most economically used and a state of maximum possible density is reached. The various modes of packing are considered by assuming the particles to be spherical. The arrangement should be such that the spheres should occupy maximum available space.

#### The packing of spheres takes place as follows:

1. When the spheres are placed in a horizontal row touching each other in such a way that the rows have a horizontal as well as vertical alignment, the spheres are found to form a square. This is called square close packing (Figure 1(a))



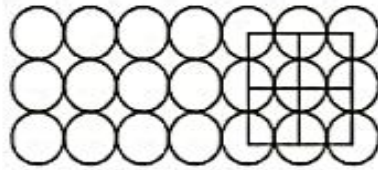


Figure I(a)

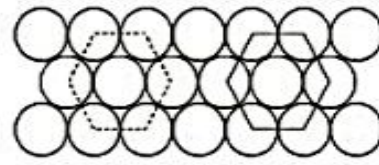


Figure I(b)

2. When the spheres are packed in such a way that the spheres in every second row are placed in the depressions between the spheres of the first row and in the third row the spheres are vertically aligned with spheres in the first row, a hexagonal close packing is obtained, since the packing of this type gives a hexagonal pattern. (Figure I (b)).

A comparison of the two ways of packing of spheres shows that in arrangement (i) the spheres are less closely packed than in arrangement (ii). It has been calculated that in arrangement (i) only 78.54% of the available space is occupied by the spheres. In the second arrangement, 90.7% of the space is occupied. Thus, arrangement (ii) is more economical and, therefore, it represents a close packing of spheres. It can be seen that in arrangement (i) each sphere is in contact with four other spheres.

On the other hand, in arrangement (ii), each sphere is in contact with six other similar spheres.

Thus, arrangement (ii) represents an efficient closest packing of spheres in a layer. We can now build other layers over the first layer to extend the packing in three dimensions. Let us mark the spheres in the first layer as A. It is clear from the following figure II(a) and figure II(b) that there are two types of voids (hollows) in the first layer. These are marked as *a* and *b*.

Now, if a second layer is placed with spheres vertically aligned with those in the first layer, its voids will come above the voids in the first layer and this would again be an inefficient way of filling the space. Obviously, for the second layer, the spheres are to be placed in either of the voids.

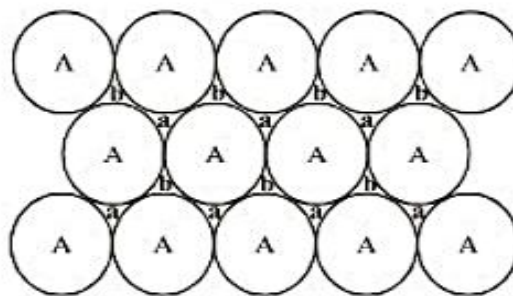
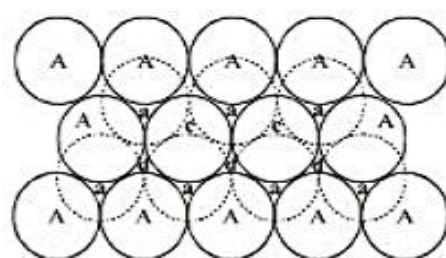


Figure II(a)

All the voids are equivalent, but the spheres of the second layer may be placed either on the voids marked '*a*' or on the other set of voids marked '*b*'. It may be noted that it is not possible to place spheres on both types of voids.

Let us place the spheres on hollows marked '*a*' to make the second layer which may be labelled as '*B*' layer. Obviously, the holes marked '*b*' remain unoccupied while building the second layer. The second layer is indicated in the following figure.



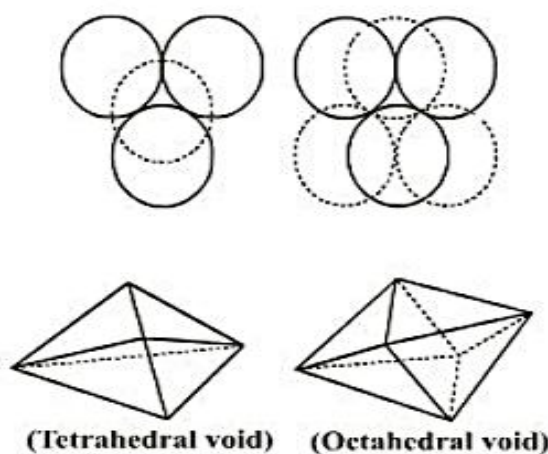


Solid circles represent layer A  
Dotted circles represent layer B  
Figure II (b)

Now, there are two types of voids in the second layer. These are marked as 'c' and 'd'. The voids 'c' (of the second layer) are ordinary voids which lie above the spheres of the first layer whereas voids 'd' lie on the voids of the first layer and hence are combination of two voids, one of the first layer and second of the second layer.

The 'a' and 'b' voids of the first layer are both triangular whereas only 'c' voids of the second layer are triangular. The 'd' voids of the second layer which are a combination of two triangular voids (one each of first and second layer) with the vertex of one triangle upwards and the vertex of other triangle downwards.

A simple triangular void in a crystal is surrounded by four spheres and is called a tetrahedral void or a hole. A double triangular void like 'd' is surrounded by six spheres and is called an octahedral void.



Now, there are two ways of building a third layer.

- (i) When a third layer is placed over the second in such a way that the spheres cover the tetrahedral or 'c' voids, a three dimensional closest packing is obtained, where the spheres in every third layer or alternate layers are vertically aligned. The arrangement is called ABAB pattern or hexagonal close packing (hcp). Mo, Mg, Zn, Cd, Be, etc. have an hcp structure.
- (ii) If the third layer is placed over the second layer in such a way that the spheres cover the octahedral or 'd' voids, a different layer 'C' is formed. In this case, every fourth layer will be vertically aligned. This arrangement is called ABCABC..... pattern or cubic close packing (ccp) Fe, Ni, Cu, Ag, Au, Pt etc. have a ccp structure.

These two arrangements are depicted in figures III and IV. Both hcp and ccp arrangements of packing are equally efficient. In these patterns, the maximum possible space (74% of the available volume) is occupied. Only 26% of the space remains empty. That is why these are referred to as close packings.

In both hcp and ccp, a sphere is in contact with 6 others in its own layer and three spheres in the layer above and three spheres in the layer below. The coordination number is 12 in both the patterns.

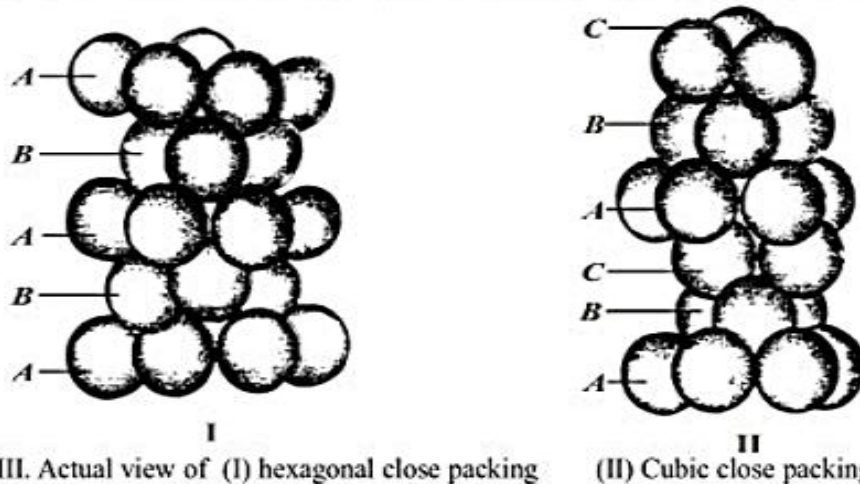


Figure III. Actual view of (I) hexagonal close packing (II) Cubic close packing

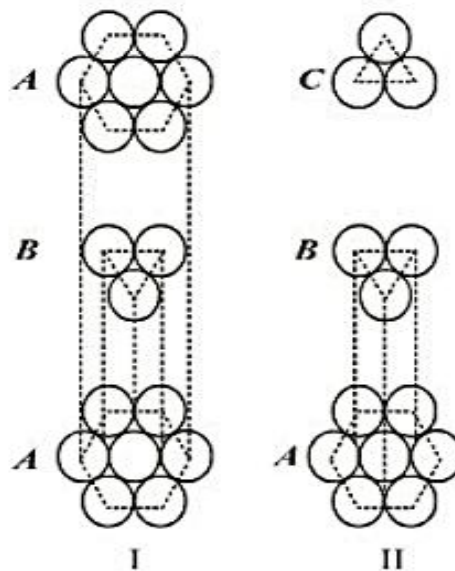


Figure IV. Simplified view of (I) Hexagonal close packing (AB AB....pattern)  
(II) Cubic close packing (ABC ABC.... pattern)

In addition to these two types of close packings, a third type of arrangement is found in metals. It is body-centered cubic packing (bcc). This is found in metals like Li, Na, K, Rb, and Cs. In this packing, the spheres are opened up and not touching. 'B' is placed on 'A'. The building of third layer is exactly like the first. The coordination number is 8 and 68% of volume is occupied.



It is seen that even in closely packed spheres and most efficient arrangements, certain hollows are left vacant. These holes or voids are called *interstitial sites*. Two important interstitial sites are (a) tetrahedral voids and (b) octahedral voids.

The voids are not tetrahedral or octahedral but the arrangement around it is such that if the spheres are arranged in the voids, the geometric figure generated is like that.

1. In the closest packed system for each sphere, there are two tetrahedral voids and only one octahedral void. The two tetrahedral voids are present above and below each atom and octahedral void is midway between two closely packed layers.
2. In ionic crystals, it is not possible for both cations and anions to have a close packed structure due to their different sizes. However, it is common for the bigger ion (usually anions) alone to approach a close-packed structure and smaller ions to fit into voids in the structure. The radii of interstitial sites that is, the voids in these close-packed structures are related to the sizes of the spheres present in them. If 'R' is the radius of the spheres in the close-packed structures, then

Radius (r) of tetrahedral void = 0.225 R

Radius (r) of octahedral void = 0.414 R.

Therefore, the limiting size of cations which can fill voids without disturbing the closest packing is for

octahedral void =  $r_c/r_a = 0.414$ , tetrahedral void =  $r_c/r_a = 0.225$ , and for cubic voids  $r_c/r_a = 0.732$

where  $r_c$  = radius of cation and  $r_a$  = radius of anion.

3. In a close-packed arrangement hcp or ccp, the number of octahedral voids are equal to the number of atoms present in the close-packed arrangement and the number of tetrahedral voids are equal to 2x (number of octahedral voids) and consequently are equal to 2x (number of atoms).

### Illustration

1. The packing fraction in fcc and hcp structure is same. Moreover, this is the highest packing fraction of all the possible unit cells with same atoms. Can you explain this?

**Sol.** The arrangement of atoms in hcp is of ABABAB ... type and in case of fcc is of ABCABCABC... type. Both in hcp and fcc, the layers are formed of same atoms in similar arrangement but the only difference is the placement of layers on top of each other. Hence, both have same packing fraction.

In both the arrangement, the number of atom of same size present around the atom is maximum, i.e., 6. So, the packing fraction is highest.

### Exercise

1. A compound formed by elements A and B crystallizes in the cubic structure where A atoms are at the corners of a cube and B atoms are at the face centres. The formula of the compound is

(A)  $AB_3$

(B) AB

(C)  $A_3B$

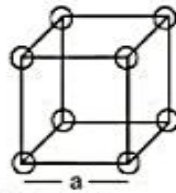
(D)  $A_2B_2$

**Ans.** (A)

### CALCULATION OF PACKING FRACTIONS

- (i) Consider a simple cubic unit cell. Suppose the edge length of the cell is  $a$  and the radius of the sphere is  $r$ . As the spheres are touching each other,  $a = 2r$ .





Number of spheres per unit cell =  $1/8 \times 8 = 1.0$

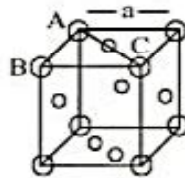
Volume of the sphere =  $\frac{4}{3} \pi r^3$

Volume of the cube =  $a^3 = (2r)^3 = 8r^3$

Packing fraction =  $\frac{\frac{4}{3} \pi r^3}{8r^3} = 0.524$  or 52.4 percent occupied.

(ii) In a face-centred cubic structure.

Spheres on the face are in contact (touching) whereas the one at corners are not touching each other.



Therefore,  $AC = 4r$

Also  $AC = \sqrt{AB^2 + BC^2}$  (since  $ABC$  is right angled triangle)

$$AC = \sqrt{a^2 + a^2}$$

$$AC = \sqrt{2}a = 4r \text{ or } a = \frac{4}{\sqrt{2}}r$$

Volume of unit cell =  $a^3 = \left(\frac{4}{\sqrt{2}}r\right)^3 = \frac{32}{\sqrt{2}}r^3$

Number of spheres in unit cell =  $\frac{1}{8} \times 8 + 6 \times \frac{1}{2} = 4$

Volume of 4 spheres =  $4 \times \frac{4}{3} \pi r^3 = \frac{16}{3} \pi r^3$

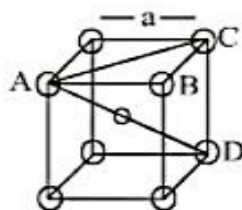
Therefore, fraction occupied =  $\frac{16\pi r^3 / 3}{32r^3 / \sqrt{2}} = 0.74$  or 74% occupied.

(iii) In a body-centred cubic structure.

$AD$  is the body diagonal and since the sphere at centre touches the one at corners,  $AD = 4r$ . Also

$$AD = \sqrt{AC^2 + CD^2}$$





$$\text{Since } AC = \sqrt{AB^2 + BC^2} = \sqrt{a^2 + a^2} = \sqrt{2}a$$

$$AD = \sqrt{2a^2 + a^2} = \sqrt{3}a = 4r$$

$$\text{Or } a = \frac{4r}{\sqrt{3}} \text{ or the volume of the cubic cell} = a^3 = \left(\frac{4r}{\sqrt{3}}\right)^3 = \frac{64r^3}{3\sqrt{3}}$$

$$\text{Number of spheres per unit cell} = \left(8 \times \frac{1}{8} = 1\right) + 1 = 2$$

$$\text{Volume of 2 spheres} = 2 \times \frac{4}{3} \pi r^3 = \frac{8}{3} \pi r^3$$

$$\text{Packing fraction} = \frac{\frac{8}{3} \pi r^3}{\frac{64r^3}{3\sqrt{3}}} = 0.68 \text{ or } 68\% \text{ occupied.}$$

## LENGTH OF UNIT CELL AND DENSITY OF A CUBIC CRYSTAL

The density of the crystal can be calculated if the edge size of the cubic crystal and the type of structure possessed by it is known.

If the length of the unit cell is  $a$

$$\text{volume of the unit cell} = a^3$$

$$\text{And, density of the unit cell} = \frac{\text{Mass of unit cell}}{\text{Volume of unit cell}} = \frac{\text{Number of atoms in the cell} \times \text{Mass of each atom}}{\text{Volume of unit cell}}$$

$$\text{Density } (\rho) = \frac{Z \times M}{a^3 \times N_a}$$

$Z$  = Effective number of atoms in unit cell

$N_a$  = Avogadro's number

$M$  = Atomic mass

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### Illustration

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1. Sodium has a bcc structure with nearest neighbour distance 365.9 pm. Calculate its density. (Atomic mass of Na = 23)

**Sol.** For the bcc structure, nearest neighbour distance ( $2r$ ) is related to edge length ( $a$ ) as

$$2r = \frac{\sqrt{3}}{2} a$$

$$\therefore a = \frac{2}{\sqrt{3}} \times 2r = \frac{2}{1.732} \times 365.9 = 422.5 \text{ pm}$$

$$M = 23$$

$$\text{For bcc structure, } z = 2 \quad d = \frac{z \times M}{a^3 \times N_0} = \frac{2 \times 23}{(422.5 \times 10^{-10})^3 \times 6.023 \times 10^{23}} = 1.51 \text{ g/cm}^3$$

1. In solid, oxide ions are arranged in ccp. One sixth of the tetrahedral voids are occupied by the cations (A) while one third of the octahedral voids are occupied by the cations (B). What is the formula of the compound. ?

**Sol.** Let, number of  $O^{2-}$  ions be 90

Then octahedral voids = 90

Tetrahedral voids = 180

Number of cations (A) =  $1/6 \times 180 = 30$

Number of cations (B) =  $1/3 \times 90 = 30$

$\therefore$  Ratio A : B :  $O^{2-}$  = 30 : 30 : 90 = 1 : 1 : 3

The formula of the compound is  $ABO_3$

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### Exercise

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1. An element crystallizes as face centred cubic lattice with density  $5.20 \text{ g/cm}^3$  and edge length of the side of unit cell as 300 pm. Calculate the mass of the element which contains  $3.01 \times 10^{24}$  atoms.

**Sol.** 105.65 g

1. A compound formed by elements X and Y, Crystallizes in the cubic structure where X is at the corners of the cube and Y is at the six face centre. What is the formula of the compound ? If side length is 5 Å, estimate the density of the solid assuming atomic weight of X and Y as 60 and 90 respectively.

**Ans.**  $4.38 \text{ gm/cm}^3$

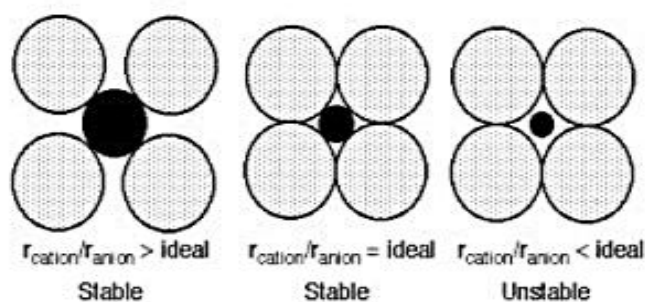
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### RADIUS RATIO RULES

Following conditions must be satisfied simultaneously during the stacking of ions of different sizes in an ionic crystal:

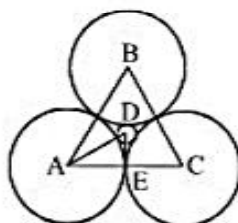
- (a) An anion and a cation are assumed to be hard spheres always touching each other.
- (b) Anions generally will not touch but may be close enough to be in contact with one another in a limiting situation.
- (c) A cation should surround itself with as many anions as possible. Each ion tends to surround itself with as many ions of opposite sign as possible to reduce the potential energy. This tendency promotes the formation of close-packed structures.

## RADIUS RATIO



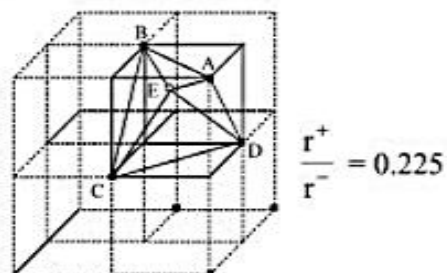
### Radius ratio for co-ordination number 3

(Triangular Arrangement):  $\frac{r^+}{r^-} = 0.155$



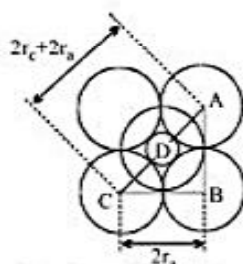
### Radius ratio for coordination number 4

(Tetrahedral arrangement):



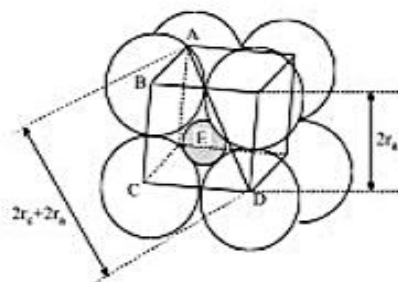
### Radius ratio for coordination number 6:

(Octahedral Arrangement)  $\frac{r^+}{r^-} = 0.414$



Top view of octahedral arrangement

**Radius ratio for coordination number 8 :  
(Body centered cubic crystal)**



$$\frac{r^+}{r^-} = 0.732$$

**Ligancy as a function of radius ratio in 1 : 1 or AB-type structure**

S.No.	Ligancy or coordination number	Range of radius ratio	Configuration	Structure type	Examples
1.	2	$0.0 < \frac{r^+}{R} < 0.155$	Linear	—	—
2.	3	$0.155 \leq \frac{r^+}{R} < 0.225$	Triangular	—	—
3.	4	$0.225 \leq \frac{r^+}{R} < 0.414$	Tetrahedral	ZnS	CuCl, CuBr, CuI, BaS, HgS
4.	6	$0.414 \leq \frac{r^+}{R} < 0.732$	Octahedral	NaCl	MgO, NaBr, CaS, MnO, KBr, CuO
5.	8	$0.732 \leq \frac{r^+}{R} < 1.0$	Cubic	CsCl	CsI, CsBr, TlBr, NH <sub>4</sub> Br
6.	12	$\frac{r^+}{R} = 1.0$	fcc or hcp	—	—

\* $r$  = radius of cation ;  $R$  = radius of anion

**Illustration**

**Q.1** A solid  $A^+ B^-$  has a sodium-chloride-type close-packed structure. If the anion has a radius of 250 pm, what should be the radius of the cation? Can a cation  $C^+$  having a radius of 180 pm be slipped into the tetrahedral site of the crystal  $A^+ B^-$ ?

**Sol.** As  $A^+ B^-$  has a sodium-chloride-type packing,  $A^+$  ions will be present in octahedral voids. The ideal radius of the cation will be equal to the radius of the octahedral void as then the cation will touch the anions and the arrangement will be close packed.

$$\text{Radius of octahedral void} = r_{A^+} = 0.414 \times r_{B^-}$$



Therefore,  $r_{A^+} = 0.414 \times 250 \text{ pm} = 103.4 \text{ pm}$

The radius of tetrahedral site is  $= 0.225 \times r_{B^-} = 0.225 \times 250 \text{ pm}$   
 $= 56.25 \text{ pm}$

Obviously, cation  $C^+$  of 180 pm dimension cannot be slipped into the tetrahedral site.

### Exercise

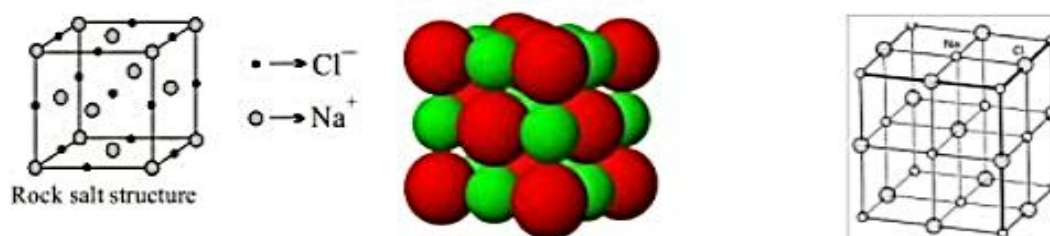
1. What is the simplest formula of a solid whose cubic unit cell has the atom A at each corner, the atom B at each face centre and C atom at the body centre  
 (A)  $AB_2C$  (B)  $A_2BC$  (C)  $AB_3C$  (D)  $ABC_3$
- Ans. (C)

### Effect of Temperature and Pressure on Crystal Structure

On applying a high pressure, sodium chloride structure (6 : 6 coordination) changes to cesium chloride structure (8 : 8 coordination). Similarly, cesium chloride structure on heating to 760 K changes to sodium chloride structure. Obviously, an increase in pressure enhances the coordination number whereas an increase in temperature causes a reverse effect.

### Structure of Some Ionic Crystals

#### Sodium Chloride (NaCl) Type AB. (Rock Salt)



$r_{Na^+} / r_{Cl^-} = 0.524$  suggests octahedral voids.

- (a) It has face-centred cubic (fcc) arrangements (also called cubic close packing ccp).  $Cl^-$  are large and present at the corners and face centres whereas  $Na^+$  (in octahedral holes) are present at the body centre and edge centre.
- (b) Since the number of octahedral holes is equal to the number of anions, the formula is NaCl. In this packing, each  $Na^+$  is surrounded by six  $Cl^-$  and each  $Cl^-$  is surrounded by 6  $Na^+$ . (In this packing, there are six octahedral holes.) Therefore, the coordination number of  $Na^+$  and  $Cl^-$  is six, that is, this structure has 6 : 6 coordination.
- (c) In the unit cell,  $Cl^-$  are at the corners and at the face centres; therefore, the number of  $Cl^-$  per unit cell is

$$8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4.$$

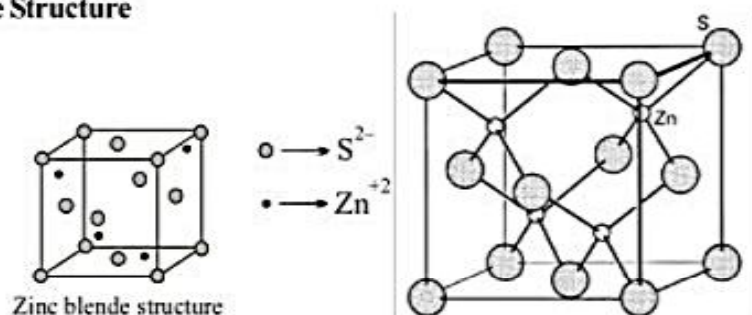
Similarly,  $\text{Na}^+$  are at the body centre and edge centre.

$$\text{Total number of } \text{Na}^+ \text{ per unit cell} = 1 + 12 \times \frac{1}{4} = 4.$$

Thus, there are four NaCl units per unit cell.

Other crystals which have a similar structure are AgCl, AgBr, oxides and sulphides of alkaline earth metals (except BeS) and halides of K, Rb and  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{Br}$  and  $\text{NH}_4\text{I}$ .

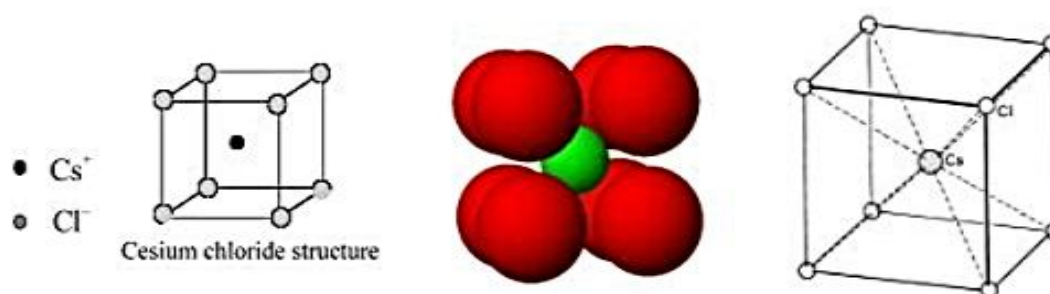
### Zinc Blende ( $\text{ZnS}$ )-Type Structure



$r_{\text{Zn}^{2+}} / r_{\text{S}^{2-}} = 0.40$ , that is, a tetrahedral arrangement.

- (a) The crystal has a cubic close packing (ccp) in which  $\text{S}^{2-}$  form a face-centred cubic structure and thus are present at the corners and at the centre of each face, whereas  $\text{Zn}^{2+}$  occupy the tetrahedral holes.
- (b) For every atom or ion closely packed, there are two tetrahedral holes and only half are occupied by  $\text{Zn}^{2+}$  to have the formula  $\text{ZnS}$  (1 : 1 stoichiometry). Only alternate holes are occupied by  $\text{Zn}^{2+}$ .
- (c) Each  $\text{Zn}^{2+}$  in a tetrahedral hole is surrounded by 4 sulphide ions and each sulphide ion is surrounded by four  $\text{Zn}^{2+}$ . Thus, the coordination number of both ions is 4 or it has 4 : 4 coordination.
- (d) In a unit cell  
 Out of 8 tetrahedral voids,  $\text{Zn}^{2+}$  occupy four.  
 Therefore, the number of  $\text{Zn}^{2+}$  per unit cell = 4.  
 Sulphide ions occupy the corners and face centres.  
 So, the number of sulphide ions is  $8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$ .  
 So, there are four ZnS units per unit cell.
- (e) BeS, AgI, and halides of copper have a similar structure.

### Caesium Chloride (CsCl)-Type Structure



- It has a body-centred cubic (bcc) arrangement plus a hole (cubic).
- $\text{Cl}^-$  form a simple cubic arrangement and occupy corners of a cube and  $\text{Cs}^+$  is present in the body in interstitial hole.
- Each  $\text{Cs}^+$  is surrounded by 8  $\text{Cl}^-$  and each  $\text{Cl}^-$  is surrounded by 8  $\text{Cs}^+$ . The coordination number is 8 : 8.
- In a unit cell,

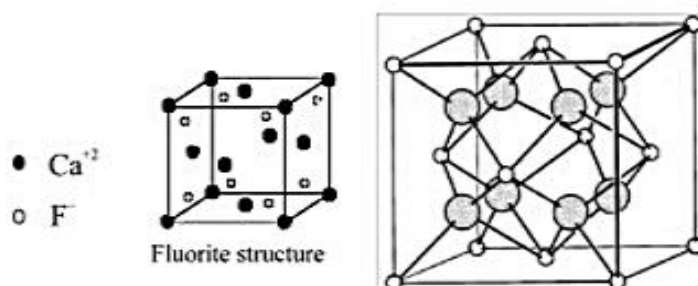
$$\text{the total number of } \text{Cl}^- \text{ is } 8 \times \frac{1}{8} = 1$$

$$\text{and the total number of } \text{Cs}^+ = 1$$

Therefore, there is one unit of Cs Cl per unit cell.

- Cs Br, Cs I, Tl Cl, Tl Br, Tl I, and Tl CN have a similar structure.

### Calcium Fluoride ( $\text{CaF}_2$ ) (Fluorite)



- This is also a ccp or fcc structure. Each  $\text{Ca}^{2+}$  is present at corners plus centre of each face.  $\text{F}^-$  occupy tetrahedral sites.
- Since there are two tetrahedral holes for each  $\text{Ca}^{2+}$ , there would be two  $\text{F}^-$  per calcium ion. The stoichiometry is 1 : 2.
- Each  $\text{Ca}^{2+}$  is surrounded by 8  $\text{F}^-$  and each  $\text{F}^-$  (in tetrahedral hole) has 4  $\text{Ca}^{2+}$  around it. Therefore, the coordination number of  $\text{Ca}^{2+}$  is 8 and that of  $\text{F}^-$  is 4, or the coordination number of the crystal is 8 : 4.
- The unit cell has



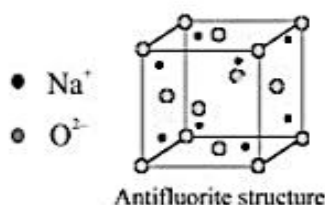
$$\text{Ca}^{2+} = 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$$

$\text{F}^- = 8$  within the body

Therefore, there are 4  $\text{CaF}_2$  units per unit cell.

- (e)  $\text{PbF}_2$ ,  $\text{BaCl}_2$ ,  $\text{BaF}_2$ ,  $\text{SrF}_2$ ,  $\text{SrCl}_2$ ,  $\text{CdF}_2$ , and  $\text{ThO}_2$  have this type of structure.

#### Antifluorite Structure (Reverse of Fluorite)



Examples are  $\text{Li}_2\text{O}$ ,  $\text{Na}_2\text{O}$ , etc.

In this, the oxide ions form a cubic arrangement and  $\text{Na}^+$  or  $\text{Li}^+$  is in tetrahedral hole. The oxide ions are surrounded by 8  $\text{Li}^+$  or  $\text{Na}^+$  whereas each  $\text{Li}^+$  or  $\text{Na}^+$  is surrounded by four oxide ions. So, the coordination number of Li or Na is 4 and that of oxide is 8 or it has 4 : 8 coordination.

Metals like Al, Ag, Au, Cu, Ni and Pt have a ccp structure and Be, Cd, Mg, Co and Zn have a hcp structure.

#### Illustration

1. The radius of a calcium ion is 94 pm and of an oxide ion is 146 pm. Predict the crystal structure of calcium oxide.

Sol. The ratio  $\frac{r^+}{r^-} = \frac{94}{146} = 0.644$

The prediction is an octahedral arrangement of the oxide ions around the calcium ion. Because the ions have equal but opposite charges, there must also be an octahedral arrangement of calcium ions around oxide ions. Thus, we would expect a rock salt ( $\text{NaCl}$ ) structure.

#### Exercise

1. Radii of  $\text{A}^+$  and that of  $\text{X}^-$  and  $\text{Y}^-$  have been given as  
 $\text{A}^+ = 1.00 \text{ pm}$   
 $\text{X}^- = 1.00 \text{ pm}$   
 $\text{Y}^- = 2.00 \text{ pm}$

Assign structure of AX and AY crystals and also determine the volume of unit cells of AX and AY crystals.

Ans. volume ( $a^3$ ) =  $216 \text{ pm}^3$



2. The density of CaO is  $3.35 \text{ gm/cm}^3$ . The oxide crystallizes in one of the cubic systems with an edge of  $4.80 \text{ \AA}$ . How many  $\text{Ca}^{2+}$  ions and  $\text{O}^{2-}$  ions belong to each unit cell, and which type of cubic system is present?

Ans. Cubic system is FCC type.

3. In LiI crystal,  $\text{I}^-$  ions form a cubical closest packed arrangement and  $\text{Li}^+$  ions occupy octahedral holes. What is the relationship between the edge-length of the unit cells and the radii of the  $\text{I}^-$  ions? Calculate the limiting ionic radii of  $\text{Li}^+$  and  $\text{I}^-$  if  $a = 600 \text{ pm}$ .

Ans.  $87.84 \text{ pm}$

Noble gases (except He, which has a hcp structure) have a ccp structure.

### Structure of $\text{FeO}$ , $\text{Fe}_2\text{O}_3$ , and $\text{Fe}_3\text{O}_4$

- (a)  **$\text{FeO}$ .** This oxide is non-stoichiometric and has a composition  $\text{Fe}_x\text{O}$  (Generally 'x' varying from 0.92 to 0.97). The oxide ions form a cubic close packing. The octahedral voids are occupied by  $\text{Fe}^{2+}$  but a small number of  $\text{Fe}^{2+}$  are replaced by  $\text{Fe}^{3+}$  ions. Three  $\text{Fe}^{2+}$  will be replaced by two  $\text{Fe}^{3+}$  to maintain electrical neutrality but then what we obtain is an iron-deficient crystal.
- (b)  **$\text{Fe}_2\text{O}_3$ .** If all  $\text{Fe}^{2+}$  are replaced by  $\text{Fe}^{3+}$ , the ratio between Fe:O will be 2 : 3 (since 3  $\text{Fe}^{2+}$  are replaced by 2  $\text{Fe}^{3+}$ ) and not 1 : 1. As such, we obtain  $\text{Fe}_2\text{O}_3$ .
- (c)  **$\text{Fe}_3\text{O}_4$ .** This is obtained by replacing exactly two thirds of  $\text{Fe}^{2+}$  by  $\text{Fe}^{3+}$  (in  $\text{FeO}$  structure). The remaining  $\text{Fe}^{2+}$  ions and 50% of  $\text{Fe}^{3+}$  ions occupy the octahedral voids. The remaining  $\text{Fe}^{3+}$  ions occupy tetrahedral voids.

If in the structure of  $\text{Fe}_3\text{O}_4$ , the  $\text{Fe}^{2+}$  ions are replaced by divalent cations such as  $\text{Mg}^{2+}$ ,  $\text{Zn}^{2+}$ , etc., the compounds obtained are called *ferrites*. In ferrites, divalent cations occupy tetrahedral voids and trivalent cations occupy octahedral voids. This structure is called *spinel structure*.

## IMPERFECTIONS IN SOLID

Any deviation from the perfectly ordered arrangement constitutes a defect or imperfection. These defects sometimes called thermodynamic defects because the number of these defects depends on the temperature. Crystals may also possess additional defect due to the presence of impurities. Imperfection not only modify the properties of solids but also give rise to new properties.

### Electronic imperfection

Generally, electrons are present in fully occupied lowest energy states. But at high temperatures, some of the electrons may occupy higher energy state depending upon the temperature.

For example, in the crystals of pure Si or Ge some electrons are released thermally from the covalent bonds at temperature above 0 K. These electrons are free to move in the crystal and are responsible for electrical conductivity. This type of conduction is known as intrinsic conduction.

The electron deficient bond formed by the release of an electron is called a hole. In the presence of electric field the positive holes move in a direction opposite to that of the electrons and conduct electricity.

### Atomic imperfection

The compounds in which the number of irregularity present in the arrangement of atoms or ions are called- atomic imperfections. It is of two types -

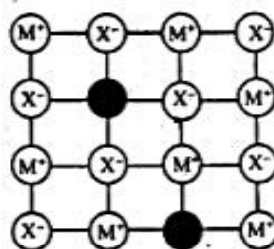
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## STOICHIOMETRIC DEFECTS

Those compounds in which the number of positive and negative ions are exactly in the ratio indicated by their chemical formula are called stoichiometric compounds. eg NaCl (1 : 1)

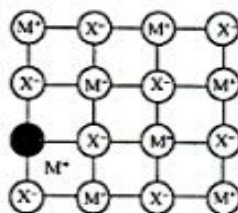
These solids show following types of defects:

- (a) **Schottky defect** : This type of defect is created when same number of positive ion and negative ion are missing from their respective positions leaving behind a pair of holes. Schottky defect is more common in ionic compounds with high co-ordination number and where the size of positive and negative ions are almost equal. The presence of large number of schottky defects in crystal results in significant decrease in its density. Eg. NaCl, KCl, CsCl, KBr etc.



Schottky Defect

- (b) **Interstitial Defect** : This type of defect is caused due to the presence of ions in the normally vacant interstitial sites in the crystal.
- (c) **Frenkel Defect** : This type of defect is created when an ion leaves its correct lattice site and occupies an interstitial site. Frenkel defects are common in ionic compounds which have low co-ordination number and in which there is large difference in size between positive and negative ions. Eg. ZnS, AgCl, AgBr, Ag etc.



Frenkel Defect

### Non Stoichiometric Defect Frenkel Defect

There are many compound in which the ratio of positive and negative ions present in the compound differs from that required by ideal formula of the compound. Such compounds are called Nonstoichiometric compounds. eg.  $\text{VO}_x$  (Where x can vary between 0.6 to 1.3.)

In these compounds balance of positive and negative charges is maintained by having extra electrons or extra positive charge.

So, these defects are of following types:

- (a) **Metal excess defects due to anion vacancies**

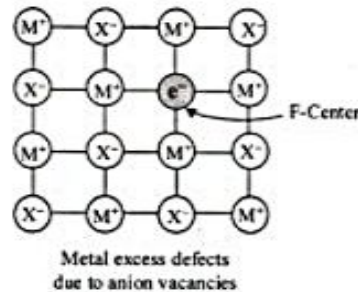
A compound may have excess metal ion if a negative ion is absent from its lattice site, leaving a hole which is occupied by electron to maintain electrical neutrality.

The holes occupied by electrons are called F-centres and are responsible for the colour of the compound.

Eg.

- The excess sodium in NaCl makes the crystal appears yellow.
  - Excess potassium in KCl makes it violet.
  - Excess lithium in LiCl makes it Pink.
-

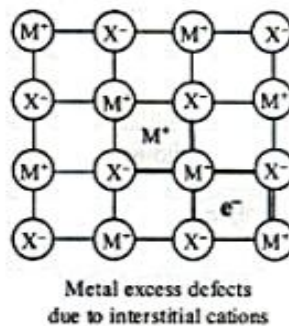
Greater the number of F-centres greater is the intensity of colour. This type of defects are found in crystal which are likely to possess schottky Defects.



**(b) Metal excess defects due to interstitial cations**

It may occur if an extra positive ion is present in an interstitial site. Electrically neutrality is maintained by the presence of an electron in the interstitial site.

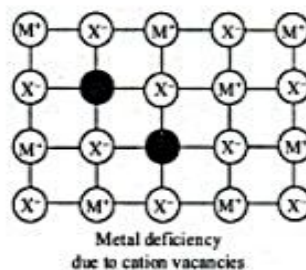
This type of defects are exhibited by the crystals which are likely to exhibit "Frenkel defects". Eg. Yellow colour of ZnS.



**(c) Metal deficiency due to cation vacancies**

The non-stoichiometric compound may have metal deficiency due to the absence of a metal ion from its lattice site. The charge is balanced by an adjacent ion having higher positive charge.

This type of defects are generally shown by compounds of transition metals.





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### Illustration

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1. Analysis shows that nickel oxide has the formula  $\text{Ni}_{0.98}\text{O}$ . What fractions of the nickel exist as  $\text{Ni}^{2+}$  and  $\text{Ni}^{3+}$ ?

**Sol.** 98 Ni atoms are associated with 100 O atoms. Out of 98 Ni atoms, suppose Ni present as  $\text{Ni}^{2+} = x$

Then Ni present as  $\text{Ni}^{3+} = 98 - x$

Total charge on  $x \text{ Ni}^{2+}$  and  $(98 - x) \text{ Ni}^{3+}$  should be equal to total charge on 100  $\text{O}^{2-}$  ions.

Hence,  $2 \times x + 3 \times (98 - x) = 100 \times 2$

or  $2x + 294 - 3x = 200$

$\therefore x = 94$

$\therefore$  Fraction of Ni present as  $\text{Ni}^{2+} = \frac{94}{98} \times 100 = 96\%$

Fraction of  $\text{Ni}^{3+}$  present as  $\text{Ni}^{3+} = \frac{4}{98} \times 100 = 4\%$

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### Exercise

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1. Calcium crystallizes in a face centred cubic unit cell with  $a = 0.556 \text{ nm}$ . Calculate the density if it contains.  
(i) 0.1% Frenkel defect  
(ii) 0.1% Schottky defect

**Ans.** (i)  $1.5463 \text{ g/cm}^3$  (ii)  $1.5448 \text{ g/cm}^3$

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## PROPERTIES OF SOLIDS

### Electrical properties of solids :

On the basis of electrical conductivity, solids are classified into three types.

*i. metals*

*ii. semi-conductors*

*iii. insulators*

Electrical conductivity of metals is very high and is of the order of  $10^6 - 10^8 \text{ ohm}^{-1} \text{ cm}^{-1}$ .

Electrical conductivity of solids is due to the movement of electrons and positive holes or through the motion of ions.

The conduction through electrons is called n-type conduction and through positive ions is called p-type conduction.

Pure ionic solids, where conduction takes place only through motion of ions, are insulators.

The presence of defects in the crystal structure increases their conductivity.

The solids whose conductivity lies between those of metallic conductors and insulators are called semi-conductors.

Semi - conductors have conductivity which lies in the range of  $10^2 - 10^9 \text{ ohm}^{-1} \text{ cm}^{-1}$ .



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The solids which do not allow the passage of electric current through them are called insulators.

Eg: Wood, rubber, sulphur, phosphorus etc..

The conductivity of semi conductors and insulators is mainly due to the presence of interstitial electrons and positive holes in the solids due to imperfections.

The conductivity of semi conductors and insulators increases with increase in temperature while that of metals decreases.

### **Magnetic properties of solids :**

The substances which are weakly repelled by magnetic field are called **diamagnetic** substances.

Eg :  $\text{TiO}_2$ , NaCl, benzene etc..

Diamagnetism arises when all the electrons are paired.

The substances which are weakly attracted by magnetic field are called **paramagnetic substances**.

Atoms, ions or molecules with unpaired electrons exhibit paramagnetism.

Paramagnetic substances lose their magnetism in the absence of magnetic field.

Eg :  $\text{TiO}$ ,  $\text{VO}_2$ ,  $\text{CuO}$  etc.

The substances which are strongly attracted by magnetic field are called **ferromagnetic substances**.

Ferromagnetic substances show permanent magnetism even in the absence of magnetic field.

Eg : Iron, cobalt, nickel,  $\text{CrO}_2$  etc.

Ferromagnetism arises due to spontaneous alignment of magnetic moments in the same direction.

Anti ferromagnetism arises due to the alignment of magnetic moments in opposite direction in a compensatory manner and resulting in a zero magnetic moment.

Eg :  $\text{MnO}$ ,  $\text{MnO}_2$ ,  $\text{Mn}_2\text{O}_3$ .

Ferrimagnetism arises due to alignment of magnetic moments in opposite directions resulting in a net magnetic moment.

Eg :  $\text{Fe}_3\text{O}_4$ ,  $\text{M}^{2+}\text{Fe}_2\text{O}_4$  ; (M = Mg, Cu, Zn etc.)

Ferromagnetic and ferrimagnetic substances change into paramagnetic substances at higher temperatures due to randomisation of spins.

### **Dielectric Properties :**

A dielectric is a substance in which an electric field gives rise to no net flow of electric charge. The electrons in a dielectric are tightly held by individual atoms.

Due to shift in charges, dipoles are created which result into polarisation.

The dipoles may align in an ordered manner such that there is some resultant dipole moment in the crystals.

The dipoles may align in such a way that the dipole moments cancel each other and resultant dipole moment is zero.

There may be no dipoles in the crystal but only ions are present.

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Depending upon the alignment of the dipoles, the properties of crystals are:

- i. Piezoelectricity      ii. Ferroelectricity      iii. Anti-ferroelectricity      iv. Pyroelectricity

**i. Piezoelectricity :**

The crystals in which the dipoles may align in an ordered way having some dipole are referred to as piezoelectrics and such crystals exhibit **piezoelectricity**.

Piezoelectric crystals act as mechanical-electrical transducers.

When these crystals are subjected to a pressure or mechanical stress, electricity is produced. These crystals are used as pickups in record players by the application of pressure.

**ii. Ferroelectricity :**

The solids, in which dipoles are spontaneously aligned in a particular direction, even in the absence of electric field, are called ferroelectric substances and the phenomenon is called ferroelectricity.

The direction of polarisation in these substances can be changed by applying electric field.

The examples are barium titanate ( $\text{Ba TiO}_3$ ), sodium potassium tartrate (Rochelle salt) and potassium dihydrogen phosphate ( $\text{KH}_2\text{PO}_4$ ).

**iii. Anti-ferroelectricity :**

If the alternate dipoles are in opposite direction, then the net dipole moment will be zero and the crystal is called anti-ferroelectric and the phenomenon is **antiferroelectricity**.

**iv. Pyroelectricity :**

Some of the polar crystals when heated produce small electric current. This phenomenon is called **pyroelectricity**.

***Super Conducting Materials***

- Super conducting materials are those which offer no resistance to the passage of electricity. Electrical resistance decreases with decrease in temperature and becomes almost zero near the absolute zero.
  - In this state, the materials become diamagnetic and are repelled by the magnets.
  - Most metals become super conducting at very low temperatures (2 - 5K).
  - The highest temperature at which superconductivity was known is 23K in alloys of niobium (e.g.  $\text{Nb}_3\text{Ge}$ ).
  - Some organic compounds also become super conducting at temperatures below 5 K.
  - Some complex metal oxides passes super conductivity at higher temperatures.
- Super conductors are used in electronics, building magnets, power transmission, levitation transportation, (trains which move in air without rails).

## SOLVED EXAMPLE

**Q.1** Fraction of total volume occupied by atoms in a simple cube is -

- (A)  $\frac{\pi}{2}$                       (B)  $\frac{\sqrt{3}\pi}{2}$                       (C)  $\frac{\sqrt{2}\pi}{6}$                       (D)  $\frac{\pi}{6}$

**Ans.** (D)

**Sol.** In a simple cubic system, number of atoms  $a = 2r$

$$\therefore \text{Packing fraction} = \frac{\text{Volume occupied by one atom}}{\text{Volume of unit cell}} = \frac{\frac{4}{3}\pi r^3}{a^3} = \frac{\frac{4}{3}\pi r^3}{(2r)^3} = \frac{\pi}{6}$$

**Q.2** In a crystal both ions are missing from normal sites in equal number. This is an example of -

- (A) F-centres                      (B) Interstitial defect                      (C) Frenkel defect                      (D) Schottky defect

**Ans.** (D)

**Sol.** Schottky defects are arisen when one positive ion and one negative ion are missing from their respective position leaving behind a pair of holes. These are more common in ionic compounds with high coordination number and having almost similar size of cations and anions.

**Q.3** Xenon crystallizes in face centre cubic lattice and the edge of the unit cell is 620 PM, then the radius of Xenon atom is -

- (A) 219.20 PM                      (B) 438.5 PM                      (C) 265.5 PM                      (D) 536.94 PM

**Ans.** (A)

**Sol.** For fcc lattice

$$4r = \sqrt{2} a \quad \text{where } a = 620 \text{ PM}$$

$$\text{or } r = \frac{1}{2\sqrt{2}} \times a = \frac{1}{2\sqrt{2}} \times 620 \text{ PM} = 219.20 \text{ PM.}$$

**Q.4** The edge length of cube is 400 PM. Its body diagonal would be -

- (A) 500 PM                      (B) 693 PM                      (C) 600 PM                      (D) 566 PM

**Ans.** (B)

**Sol.** Since in body centre cubic, the body diagonal

$$= \sqrt{3} a = \sqrt{3} \times 400 \text{ PM} = 692.82 \text{ PM or say } 693 \text{ PM}$$

**Q.5** A compound alloy of gold and copper crystallizes in a cube lattice in which the gold atoms occupy the lattice points at the corners of cube and copper atoms occupy the centres of each of the cube faces. The formula of this compound is -

- (A) AuCu                      (B) AuCu<sub>2</sub>                      (C) AuCu<sub>3</sub>                      (D) None

**Ans.** (C)

**Sol.** One-eighth of each corner atom (Au) and one half of each face centered atom (Cu) are contained within the unit cell of the compound.

$$\text{Thus, the number of Au atoms per unit cell} = 8 \times \frac{1}{8} = 1 \text{ and}$$

$$\text{the number of Cu atoms per unit cell} = 6 \times \frac{1}{2} = 3. \text{ The formula of the compound is AuCu}_3.$$



**Q.6** Lithium borohydride ( $\text{LiBH}_4$ ), crystallises in a orthorhombic system with 4 molecules per unit cell. The unit cell dimensions are :  $a = 6.81 \text{ \AA}$ ,  $b = 4.43 \text{ \AA}$ ,  $c = 7.17 \text{ \AA}$ . If the molar mass of  $\text{LiBH}_4$  is  $21.76 \text{ g mol}^{-1}$ . The density of the crystal is -

- (A)  $.668 \text{ g cm}^{-3}$  (B)  $.585 \text{ g cm}^{-2}$  (C)  $1.23 \text{ g cm}^{-3}$  (D) None

**Ans.** (A)

**Sol.** We know that,

$$\rho = \frac{ZM}{N_A V} = \frac{4 \times (21.76 \text{ g mol}^{-1})}{(6.023 \times 10^{23} \text{ mol}^{-1})(6.81 \times 4.43 \times 7.17 \times 10^{-24} \text{ cm}^3)} = 0.668 \text{ g cm}^{-3}$$

**Q.7** The unit cell of a metallic element of atomic mass  $108 \text{ gm/mole}$  and density  $10.5 \text{ g/cm}^3$  is a cube with edge length of  $409 \text{ pm}$ . The structure of the crystal lattice is -

- (A) fcc (B) bcc (C) hcp (D) None

**Ans.** (A)

**Sol.**  $\rho = \frac{Z \times M}{N_A \times a^3}$

Here,  $M = 108$ ,  $N_A = 6.023 \times 10^{23}$

Put on these values and solving we get -

$a = 409 \text{ pm} = 4.09 \times 10^{-8} \text{ cm}$ ,  $\rho = 10.5 \text{ g/cm}^3$

$Z = 4$  = number of atoms per unit cell

So, The structure of the crystal lattice is fcc.

**Q.8** Copper metal has a face-centred cubic structure with the unit cell length equal to  $0.361 \text{ nm}$ . Picturing copper ions in contact along the face diagonal. The apparent radius of a copper ion is -

- (A)  $0.128 \text{ nm}$  (B)  $1.42 \text{ nm}$  (C)  $3.22 \text{ nm}$  (D)  $4.22 \text{ nm}$

**Ans.** (A)

**Sol.** For a face-centred cube, we have

$$\text{Radius} = \frac{\sqrt{2}a}{4} = \frac{\sqrt{2} \times 0.361}{4} \text{ nm} = 0.128 \text{ nm}.$$

**Q.9** The unit cell cube length for  $\text{LiCl}$  ( $\text{NaCl}$  structure) is  $5.14 \text{ \AA}$ . Assuming anion-anion contact, calculate the ionic radius for chloride ion.

**Sol.** In a face centred cubic lattice, anions touch each other along the face diagonal of the cube.

$$4r_{\text{Cl}^-} = \sqrt{2} \times a$$

$$\therefore r_{\text{Cl}^-} = \frac{\sqrt{2}}{4} \times a$$

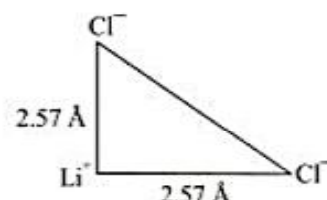
$$= \frac{\sqrt{2}}{4} \times 5.14 = 1.82 \text{ \AA}$$

Alternatively

$$\text{Distance between } \text{Li}^+ \text{ and } \text{Cl}^- \text{ ion} = \frac{5.14}{2} = 2.57 \text{ \AA}$$

$$\text{This distance between two chloride ions} = \sqrt{(2.57)^2 + (2.57)^2} = 3.63$$

$$\therefore r_{\text{Cl}^-} = \frac{3.63}{2} = 1.82 \text{ \AA}$$





- Q.10** The density of potassium bromide crystal is  $2.75 \text{ gm/cm}^3$  and the length of an edge of unit cell is  $654 \text{ pm}$ . The unit cell of KBr is one of the three types of cubic unit cells. How many of formula units of KBr are there in a unit cell? Does the unit cell have a NaCl or LiCl structure?

**Sol.** 
$$\rho = \frac{Z \times M}{N_0 \times a^3}$$

$$\therefore Z = \frac{d \times a^3 \times N_0}{M}$$

$$= \frac{2.75 \times (654 \times 10^{-10})^3 \times 6.023 \times 10^{23}}{119}$$

$$= 3.89 \approx 4$$

Number of formula units = 4  
It is NaCl type crystal (FCC)

- Q.11** A metal (atomic mass = 50) has a body centre cubic crystal structure. The density of the metal is  $5.96 \text{ g/cm}^3$ . Find the volume of unit cell. ( $N_0 = 6.023 \times 10^{23} \text{ atoms mol}^{-1}$ )

**Sol.** Mass of the unit cell = mass of one atom  $\times$  No. of atom present per unit cell  $= \frac{50}{6.023 \times 10^{23}} \times 2$

$$\text{Volume of unit cell} = \frac{\text{Mass}}{\text{Density}}$$

$$= \frac{50 \times 2}{6.023 \times 10^{23}} \times \frac{1}{5.96} = 2.78 \times 10^{-23} \text{ cm}^3$$

- Q.12** The unit cell length of NaCl is observed to be  $0.5627 \text{ nm}$  by X-ray diffraction studies; the measured density of NaCl is  $2.164 \text{ cm}^{-3}$ . Calculate the different of observed and calculated density and calculate % of missing  $\text{Na}^+$  and  $\text{Cl}^-$  ions.

**Sol.** Density ( $\rho$ )  $= \frac{Z \times M}{N_0 \times a^3}$

$$= \frac{4 \times 58.5}{6.023 \times 10^{23} \times (0.5627 \times 10^{-7})^3}$$

$$= 2.1805 \text{ g/cm}^3$$

Observed density =  $2.164 \text{ g/cm}^3$  which is less than calculated density because some ions are missing.  
Actual constant units per unit cell can be calculated as :

$$Z = \frac{\rho \times N_0 \times a^3}{M} = \frac{2.164 \times 6.023 \times 10^{23} \times (0.5627 \times 10^{-7})^3}{58.5} = 3.969$$

Missing units =  $4 - 3.969 = 0.031$

$$\therefore \% \text{ missing of } \text{Na}^+ \text{ and } \text{Cl}^- = \frac{0.031}{4} \times 100 = 0.775\%$$

**Q.13** Compute the percentage void space per unit volume of unit cell in zinc fluoride structure.

**Sol.** Since anions occupy fcc position and half of the tetrahedral voids are occupied by cations, there are 4 anions and 8 tetrahedral voids per unit cell. The fraction of volume occupied by spheres per unit volume of the unit cell is

$$= \frac{4 \times \left( \frac{4}{3} \pi r_a^3 \right) + \frac{1}{2} \times 8 \times \left( \frac{4}{3} \pi r_c^3 \right)}{16\sqrt{2}r_a^3} = \frac{\pi}{3\sqrt{2}} \left\{ 1 + \left( \frac{r_c}{r_a} \right)^3 \right\}$$

$$= \frac{\pi}{3\sqrt{2}} \{ 1 + (-0.225)^3 \} = 0.7496 \left( \text{For tetrahedral voids, } \frac{r_c}{r_a} = 0.225 \right)$$

$\therefore$  Void volume =  $1 - 0.7496 = 0.2504$ /unit volume of unit cell

% void space = 25.04%

**Q.14** Copper has fcc crystal structure. Assuming an atomic radius of 130 pm for copper atom ( $\text{Cu} = 63.54$ )

(a) What is the length of unit cell of Cu ?

(b) What is the volume of the unit cell ?

(c) How many atoms belong to the unit cell ?

(d) Find the density of Cu

**Sol.** As we know

$$\rho = \frac{n \times M_m}{N_0 \times a^3}$$

(a) For FCC structure

$$4r = \sqrt{2} a$$

$$a = 2 \sqrt{2} r$$

$$= 2 \sqrt{2} \times 130 \text{ pm} = 367.64 \text{ pm}$$

(c) Volume of unit cell  $a^3 = \frac{n \times M_m}{N_0 \times \rho} = (3.67 \times 10^{-8})^3 = 4.94 \times 10^{-23} \text{ cm}^3$

(c)  $n = 4$

(d)  $\rho = \frac{4 \times 63.54}{6.03 \times 10^{23} \times (3.67 \times 10^{-8})^3} = 8.54 \text{ gm/cm}^3$

**Q.15** A metal crystallizes in two cubic phases, face centre cubic (fcc) and body centred cubic (bcc) whose unit cell length are 3.5 and 3.0 Å respectively. Calculate the ratio of density of fcc and bcc.

**Sol.**  $\rho = \frac{n \times M_m}{N_0 \times a^3}$

For FCC

$n = 4, a = 3.5 \text{ Å}$

$\therefore \rho(\text{fcc}) = \frac{4 \times M_m}{N_0 \times (3.5)^3} \dots\dots(i)$

For bcc lattice  
 $n = 2, a = 3.0 \text{ \AA}$

$$\rho_{\text{bcc}} = \frac{2 \times M_m}{N_A \times (3.0)^3} \quad \dots(ii)$$

Comparing eqs. (i) and (ii), we get

$$\therefore \frac{\rho_{\text{fcc}}}{\rho_{\text{bcc}}} = \frac{4}{2} \times \frac{3^3}{(3.5)^3} = \frac{4 \times 3 \times 3 \times 3}{2 \times 3.5 \times 3.5 \times 3.5} = 1.259$$

**Q.16** Prove that void space in fluorite structure per unit volume of unit cell is 0.251.

**Sol.** Cations form cubical closest packing and anions occupying the tetrahedral holes.  
There are 4 cations and 8 anions per unit cell.

Here, face diagonal

$$4r^+ = \sqrt{2} a$$

where,  $r^+$  = radius of cation

$$\therefore a = 2 \sqrt{2} r^+$$

$$\therefore a^3 = (2 \sqrt{2} r^+)^3$$

$$\text{Volume of unit cell} = 16 \sqrt{2} (r^+)^3$$

Fraction of volume occupied per unit volume of unit cell

$$\text{i.e. Packing fraction} = \frac{4 \times \left( \frac{4}{3} \pi r^{3+} \right) + 8 \times \left( \frac{4}{3} \pi r^{3-} \right)}{16 \sqrt{2} r^{3+}}$$

$$= \frac{\pi}{3 \sqrt{2}} \left[ 1 + \left( \frac{2r^{3-}}{r^{3+}} \right) \right]$$

Here in fluorite structure, for tetrahedral hole

$$\frac{\text{Radius of anion}}{\text{Radius of cation}} = \frac{r^-}{r^+} = 0.225$$

$$\text{Packing fraction} = \frac{\pi}{3 \sqrt{2}} \{ 1 + 2(0.225)^3 \} = 0.749$$

$$\therefore \text{Void space} = 1 - 0.749$$

$$\text{Void fraction} = 0.251$$



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## SURFACE CHEMISTRY

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The phenomenon of attracting and retaining the molecules of a substance on the surface of a liquid or solid resulting into a higher concentration of molecules on the surface is called *adsorption*. The substance adsorbed on the surface is called *adsorbate* and the substance on which it is adsorbed is called *adsorbent*. The surface where the process takes place is known as *interface*.

### Examples :

1. Dyes get adsorbed on cotton fibres, activated carbon, etc.
2. Ammonia gas placed in contact with charcoal gets adsorbed on it.
3. Oxalic acid placed in contact with activated carbon gets adsorbed on it.

### Positive and Negative Adsorption

**Positive adsorption :** In case of adsorption by solids from the solutions, mostly the solute is adsorbed on the surface of the solid adsorbent so that the concentration of solute on the surface of the adsorbent is greater than in the bulk. This is known as positive adsorption. Hence when the concentration of the adsorbate is more on the surface of the adsorbent than in the bulk, it is known as positive adsorption.

**Negative adsorption:** In some cases, the solvent from the solution may be adsorbed by the adsorbent so that the concentration of the solution increases than the initial concentration. This is called negative adsorption. Hence if the concentration of the adsorbate is less on the surface of the adsorbent than in the bulk, it is known as negative adsorption.

### Factors Affecting Adsorption

1. **Nature and surface area of the adsorbent :** If the surface is polar or activated, that is, some active groups are present at the surface, it is favourable for adsorption. Similarly, if the surface area of the adsorbent is large, the amount of adsorption would be more. That is why finely divided substances have a larger adsorption power than when they are present in a compact form.
2. **Nature of adsorbate :** Whether the adsorbent is a gas or a solute present in a solution, factors like structure and dimensions of the molecule and presence of some polar group affect adsorption.
3. **Temperature :** Normally, adsorption decreases with an increase in temperature; however, it can be vice versa as well.
4. **Concentration/Pressure:** At constant temperature, adsorption increases with an increase in concentration or pressure of the adsorbate.

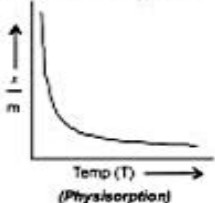
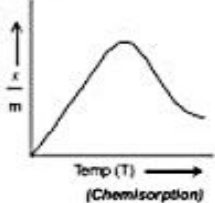
### There are two main types of adsorption

1. **Physical adsorption/ van der Waal's adsorption/ Physisorption.** When molecules are held at the surface by van der Waal's forces (which are weak intermolecular forces of attraction) without resulting in the formation of any chemical bond between the adsorbate and adsorbent, it is called physical adsorption. It is a reversible process. Also, a decrease in temperature increases the adsorption.
-



2. **Chemical adsorption/Chemisorption.** When the adsorbate molecule is held on the surface of a solid by forces similar to those of a chemical bond, the type of adsorption is called chemical adsorption or chemisorption. The heat released during chemisorption is high and the process is normally irreversible. Another important aspect is that physical adsorption is non-specific in nature whereas chemical adsorption is specific in nature and occurs when there is a tendency towards the formation of some sort of bond between the adsorbate and adsorbent molecule.

### COMPARISON OF PHYSI-SORPTION AND CHEMISORPTION

S.No.	Physical adsorption	Chemical adsorption
1.	It is caused by intermolecular van der Waals' forces.	It is caused by chemical bond formation.
2.	It is not specific.	It is highly specific.
3.	It is reversible.	It is irreversible.
4.	It depends on the nature of gas. More easily liquefiable gases are adsorbed readily.	It depends on the nature of gas. Gases which form compounds with the adsorbent exhibit chemisorption.
5.	Heat of adsorption is low due to weak forces. (4–40 kJ/mole)	Heat of adsorption is high due to strong attractive forces (40–400 kJ/mole)
6.	Low temperature is favourable. It decreases with increase of temperature. 	High temperature is favourable. It increases with increase of temperature. 
7.	No appreciable activation energy is involved.	High activation energy is involved.
8.	High pressure is favourable. Decrease of pressure causes desorption.	High pressure is favourable. Decrease of pressure does not cause desorption.
9.	It depends on the surface area. It increases with increase of surface area.	It also depends on the surface area. It increases with increase of surface area.
10.	It forms multilayers on adsorbent surface under high pressure.	It forms unimolecular layer.

### Characteristics of Adsorption

1.  $x/m$ , that is, amount adsorbed per gram of adsorbent ( $x$  = amount adsorbed and  $m$  = amount of adsorbent) depends on the chemical nature of both the adsorbent and adsorbate and also on their physical state.
2.  $x/m$  depends on the equilibrium concentration or pressure of the adsorbate and temperature.
3. Adsorption can be reversible or irreversible.
4. Adsorption is generally followed by a decrease in enthalpy and entropy both.
5. Adsorption can be selective and specific or non-specific.

### Thermodynamics of Adsorption :

Adsorption is spontaneous process, so for the process  $\Delta G$  is negative. According to Gibbs equation.

$$\Delta G = \Delta H - T\Delta S$$

For adsorption  $\Delta S$  (Change in entropy) is always negative because adsorption of molecules on the surface lowers the disorder. So, for value of  $\Delta G$  to be negative,  $\Delta H$  must necessarily be negative and  $|\Delta H| > |T \Delta S|$ . The process is exothermic because it involves forces of attraction between adsorbate and adsorbent.

As the process of adsorption proceeds further  $\Delta H$  becomes less and less after certain time period. When  $\Delta H$  becomes equal to  $T \Delta S$ ,  $\Delta G = 0$  and system attains equilibrium. At equilibrium,

$$\text{Rate of adsorption} = \text{Rate of desorption}$$

### Illustration

1. 50 mL of 1 M oxalic acid (molecular mass = 126) is shaken with 0.5 g of wood charcoal. The final concentration of the solution after adsorption is 0.5 M. Calculate the amount of oxalic acid adsorbed per gram of charcoal

**Sol.** Calculation of initial amount of oxalic acid in 50 mL solution. 1 M oxalic acid solution means 1 mole of oxalic acid (126 g) present in 1000 mL solution.

$$\therefore 50 \text{ mL of 1 M solution will contain oxalic acid} = \frac{126}{1000} \times 50 = 6.3 \text{ g}$$

Calculation of amount of oxalic acid in 50 mL solution after adsorption. Concentration of solution after adsorption = 0.5 M. Thus, 1000 mL of the solution contain oxalic acid = 0.5 mol = 63 g

$$\therefore 50 \text{ mL of the solution will contain oxalic acid} = \frac{63}{1000} \times 50 = 3.15 \text{ g}$$

Calculation of amount adsorbed per gram

$$\text{Amount of oxalic acid adsorbed by 0.5 charcoal} = 6.30 - 3.15 \text{ g} = 3.15 \text{ g}$$

$$\therefore \text{amount of oxalic acid adsorbed per gram of charcoal} = 6.30 \text{ g}$$

### Exercise

1. The following data were obtained for the adsorption of CO on 3 g of charcoal at 0°C

Pressure, P (mm)	:	180	540
Volume of gas adsorbed, x (cc) reduced to S.T.P.	:	16.5	38.1

Calculate the values of the constants k and n used in Freundlich equation.

**Ans.**  $0.1044 \text{ cm}^3 \text{ g}^{-1}$  (when pressure is in mm)

## ADSORPTION ISOTHERMS

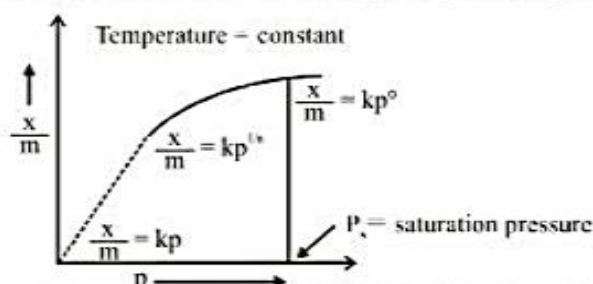
A relation between  $x/m$  (amount adsorbed per unit weight of adsorbent) and the equilibrium concentration or pressure at a fixed temperature is called *adsorption isotherm*. This is experimentally obtained by determining  $x/m$  as a function of 'c' or 'p'. Two such isotherms (empirical relation) are given below.

1. **Freundlich Adsorption Isotherm** : It is represented as

$$\frac{x}{m} = k C^{1/n} \text{ or } \frac{x}{m} = k P^{1/n}, \text{ depending on whether the adsorbate is a solution or a gas.}$$



Where  $x$  = amount of adsorbate,  $m$  = amount of adsorbent  $P$  = pressure,  $k$  and  $n$  are constants which depend on the nature of the adsorbent and the gas at given temperature.



The graph obtained gives following information about extent of adsorption.

(a) **At very low pressure :** At very low pressures, the graph is nearly straight line and at these pressures.

$$\frac{x}{m} \propto P \quad \text{or} \quad \frac{x}{m} = k.P$$

(b) **At intermediate range of pressure :** At these pressures graph is curved and

$$\frac{x}{m} \propto P^{1/n} \quad \text{or} \quad \frac{x}{m} = k.P^{1/n} \quad (\text{probable 'n' value is } 0.1 - 0.5)$$

(c) **At very high pressure :** The graph becomes parallel to x-axis which indicates that extent of adsorption is independent to the pressure i.e.,

$$\frac{x}{m} \propto P^0 \quad \text{or} \quad \frac{x}{m} = k$$

## 2. Langmuir adsorption isotherm :

Another isotherm derived by Langmuir considers the formation of only a mono-molecular layer of adsorbate on adsorbent. It is known as *Langmuir adsorption isotherm* and is based on the following points:

- It takes place on the surface of solids till a unimolecular layer is formed.
- Adsorption is a result of condensation of adsorbate molecules on solid surface and their evaporation.
- At equilibrium, the rate of condensation becomes equal to the rate of evaporation.

Based on these aspects, Langmuir derived the expression given below:

$$\frac{x}{m} = \frac{ap}{1+bp}$$

The values of constants 'a' and 'b' depend upon the nature of adsorbate, nature of solid adsorbent, and temperature. 'p' is equilibrium pressure.

Langmuir theory has limitations. This theory of unimolecular adsorption is valid only at a low pressure and high temperature. As the pressure is increased or temperature is lowered, additional layers start forming. This leads to multilayer adsorption.

### Applications of Adsorption :

- In making gas masks :** In gas masks, activated charcoal preferentially adsorbs the harmful gases like,  $\text{CH}_4$ ,  $\text{CO}$ ,  $\text{Cl}_2$  etc.
- In decolorisation processes :** for decolorisation of sugar cane juice, it is passed over activated animal charcoal, where colouring matter gets adsorbed on the surface of charcoal.

3. **In making moisture free atmosphere :** Silica gel, alumina etc are used to remove moisture as they adsorb water. That is why, small packets of silica gel are kept with delicate instruments.
4. **In production of high vacuum :** In an evacuated vessel, an adsorbent is added to remove small amounts of gases and this produces high vacuum.
5. **Chromatography :** A technique used for separation of substances is based on adsorption process.
6. **In purification of water :** Ions from water may be removed by ion-exchange resins and the process involves adsorption.
7. **In the extraction of metals :** Froth floatation process used for the concentration of ores is based on preferential adsorption of ore particles.
8. **Adsorption indicators :** Some dyes like, eosin, fluorescein etc. get adsorbed on the surface of precipitates and this property serves as basis for adsorption indicators.

### Illustration

1. Applying Freundlich adsorption isotherm, calculate the amount of acetic acid adsorbed by 1 kg of blood charcoal at 25° C from a 5% vinegar solution (mass/volume). Given that if the concentration is expressed in molarity ( $\text{mol dm}^{-3}$ ),  $x/m$  is mass of the solute adsorbed per gram of adsorbent, then  $k = 0.160$  and  $n = 2.32$ .

**Sol.** According to Freundlich adsorption isotherm,  $\frac{x}{m} = k C^{1/n}$  .....(i)

5% vinegar (acetic acid solution) means 5 g of acetic acid are present in 100 mL of the solution

Molar mass of acetic acid ( $\text{CH}_3\text{COOH}$ ) =  $60 \text{ g mol}^{-1}$

$$\therefore 5 \text{ g of acetic acid} = \frac{5}{60} \text{ mol}$$

$$\therefore 1000 \text{ mL of the solution will contain acetic acid} = \frac{5}{60} \times \frac{1}{100} \times 1000 = 0.837 \text{ mol.}$$

i.e. Concentration of the solution ( $C$ ) =  $0.837 \text{ mol L}^{-1}$

$$\frac{x}{m} = 0.160 \times (0.837)^{1/2.32}$$

$$\therefore \log \frac{x}{m} = \log (0.160) + \frac{1}{2.32} \log (0.837) = -0.7959 + 0.435 (-0.0773) = -0.8295$$

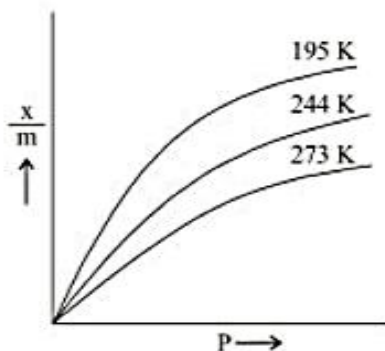
$$\therefore \frac{x}{m} = \text{Antilog} (-0.8295) = 0.1481 \text{ g (g charcoal)}^{-1}$$

$$\therefore \text{Amount adsorbed by 1 kg (1000 g) of charcoal} = 148.1 \text{ g}$$



### Exercise

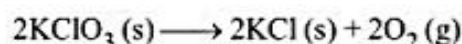
1. Consider the adsorption isotherms given on the side and interpret the variation in the extent of adsorption ( $x/m$ ) when



- (a) (i) temperature increases at constant pressure  
(ii) pressure increases at constant temperature
- Ans. (a) (i) As temperature increases at constant pressure, adsorption ( $x/m$ ) decreases  
(ii) As pressure increases at constant temperature, first adsorption increases upto a particular pressure and then it remains constant, i.e., becomes independent of pressure.
- (b) Finely divided iron is used as catalyst and molybdenum is used as promoter

## CATALYSIS

Potassium chlorate, when heated strongly ( $380^{\circ}\text{C}$ – $600^{\circ}\text{C}$ ), decomposes slowly as



However, when a small amount of manganese dioxide ( $\text{MnO}_2$ ) is added, the decomposition takes place at a considerably lower temperature range ( $200^{\circ}\text{C}$ – $360^{\circ}\text{C}$ ) and at a much considerable rate. The added  $\text{MnO}_2$  remain unchanged with respect to its mass and composition.

The systematic study of the effect of different foreign substances on the rates of chemical reactions was made by Berzelius, in 1835. He named these foreign substances as **catalyst**.

Substances, which alter the rate of a chemical reaction and themselves remain chemically and quantitatively unchanged after the reaction, are known as **catalysts** and the phenomenon is known as **catalysis**.

### CHARACTERISTICS OF CATALYTIC REACTIONS

- (i) The catalyst remains unchanged in amount and chemical composition at the end of the reaction.  
However, it may undergo considerable change in physical properties like physical state, colour etc..
- (ii) A small quantity of the catalyst is normally capable of producing the desired effect. However, in some reactions, the rate depends on the amount of catalyst. For example, the rate of inversion of cane sugar catalysed by  $\text{H}^+$  ion changes with the change in  $\text{H}^+$  ion concentration.

(iii) The catalyst is generally specific in its action. For example, the decomposition of  $\text{KClO}_3$  is catalysed by  $\text{MnO}_2$  but not by platinum. On the other hand,  $\text{MnO}_2$  can catalyse the decomposition of  $\text{KClO}_3$  but not  $\text{KClO}_4$  or  $\text{KNO}_3$ .

(iv) The catalyst does not initiate a reaction; it merely accelerates the reaction that is already occurring.

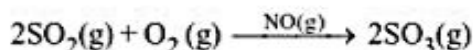
(v) A catalyst does not alter the final state of equilibrium in a reversible reaction.

### TYPES OF CATALYSIS

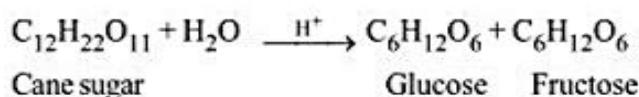
#### (a) Homogeneous Catalysis :

When the reactants and the catalyst are in the same physical state, i.e. in the same phase, it is called homogeneous catalysis. For example.

(i) **Lead chamber process:-** In this process for the manufacture of sulphuric acid,  $\text{NO}(\text{g})$  is used as a catalyst.

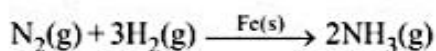


(ii) **Inversion of cane sugar:-** Inversion (hydrolysis) of sugar is catalysed by  $\text{H}^+$  ions.

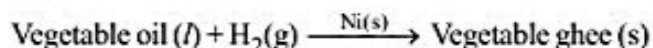


(b) **Heterogeneous catalysis:** When the catalyst and the reactants are not in the same physical state i.e. not in the same phase, it is called heterogeneous catalysis. for example.

(i) **Haber's process for  $\text{NH}_3$  formation:**

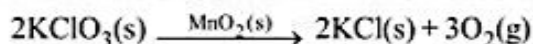


(ii) **Hydrogenation of vegetable oils** in the presence of finely divided nickel as catalyst.

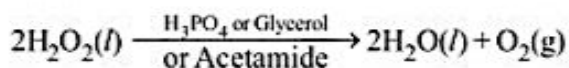
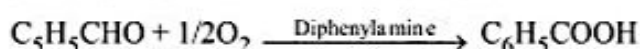
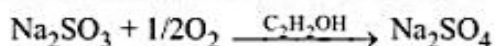


### TYPES OF CATALYSTS

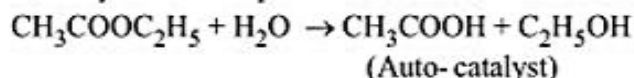
(i) **Positive catalyst (or catalyst):-** The substance which increases the rate of a reaction is known as a positive catalyst. Normally the term catalyst is used for positive catalyst. For example:



(ii) **Negative catalyst (or inhibitor) :-** The substance which decreases the rate of chemical reaction is called negative catalyst or inhibitor. For example:



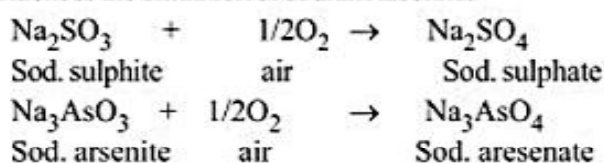
**(iii) Autocatalysts:-** When one of the products of the reaction begins to act as a catalyst, it is called auto-catalyst. For example:



In the initial stages, the reaction is slow but as soon as the products come into existence, the reaction rate increases.

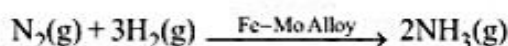
**(iv) Induced catalyst:-** When a chemical reaction enhances the rate of another chemical reaction, it is called induced catalysis. For example :

Sodium arsenite solution is not oxidised by air. If, however, air is passed through a mixture of  $\text{Na}_3\text{AsO}_3$  and  $\text{Na}_2\text{SO}_3$ , both of them undergo simultaneous oxidation. The oxidation of sodium sulphite, thus influences the oxidation of sodium arsenite.



**Promoters:-** Those substance which do not themselves act as catalysts but their presence increases the activity of a catalyst are called catalytic promoters or catalyst for a catalyst. For example:

In the Haber process for the synthesis of ammonia, Fe is the catalyst while molybdenum (Mo) acts as a promoter.



**Catalytic Poison:-** The substance whose presence decreases or destroy the activity of a catalyst is called catalytic poison. For example :

Carbon monoxide or  $\text{H}_2\text{S}$  in hydrogen gas, acts as a poison for Fe catalyst in the Haber process for  $\text{NH}_3$ ,  $\text{As}_2\text{O}_3$  acts as poison for Pt asbestos in contact process for  $\text{H}_2\text{SO}_4$ .



## THEORIES OF CATALYSIS

It is not possible to give a uniform explanation of the mechanism of the phenomenon of catalysis, as catalytic reactions are of various nature. However, the following are two basic theories of catalysis.

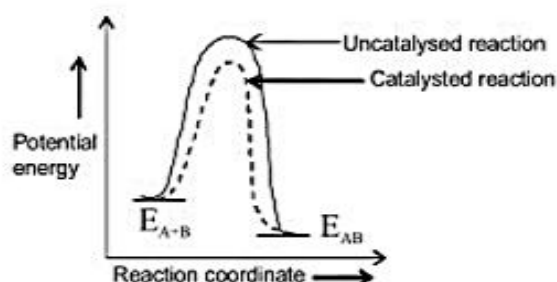
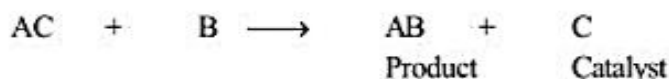
### (i) Intermediate compound formation theory

According to this theory, the catalyst first forms an intermediate compound with one of the reactants. The intermediate compound is formed with less energy consumption than needed for the actual reaction. The intermediate compound being unstable combines with other reactant to form the desired product and the catalyst is regenerated.

Consider, a reaction of the type  $\text{A} + \text{B} \xrightarrow{\text{C}} \text{AB}$  which occurs in presence of a catalyst C, may take place as

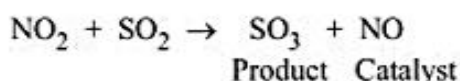
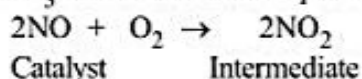






**Thus, a catalyst increases the rate of a reaction by providing a pathway whose activation energy is lower than the activation energy of the uncatalyzed reaction.**

Many catalytic reactions can be explained on the basis of this theory. Consider the catalytic oxidation of  $\text{SO}_2$  to  $\text{SO}_3$  in the lead chamber process ( $\text{NO}$  is taken as catalyst). This occurs as follows



This theory explains why the catalyst remains unchanged in mass and chemical composition at the end of the reaction and is effective even in small quantities.

## (ii) Adsorption Theory

This theory explains the mechanism of heterogeneous catalysis. The old point of view was that when the catalyst is in solid state and the reactants are in gaseous state or in solutions, the molecules of the reactants are adsorbed on the surface of the catalyst. The increased concentration of the reactants on the surface influences the rate of reaction. Adsorption being an exothermic process, the heat of adsorption is taken up by the surface of the catalyst, which is utilised in enhancing the chemical activity of the reacting molecules. The view does not explain the specificity of a catalyst.

The modern adsorption theory is the combination of intermediate compound formation theory and the old adsorption theory. The catalytic activity is localised on the surface of the catalyst. The mechanism involves five steps:

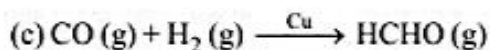
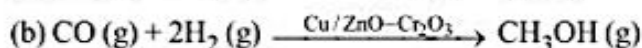
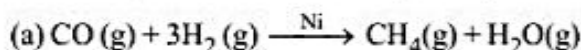
- (i) Diffusion of reactants to the surface of the catalyst.
- (ii) Adsorption of reactant molecules on the surface of the catalyst.
- (iii) Occurrence of chemical reaction on the catalyst surface, through formation of an intermediate.
- (iv) Desorption of reaction products away from the catalyst surface.
- (v) Diffusion of reaction products away from the catalyst surface.

## IMPORTANT FEATURES OF SOLID CATALYSIS :

(i) **Activity** : The activity of a catalyst depends upon the strength of chemisorption. The reactants must get adsorbed reasonably strongly on the catalyst to become active but not so strongly that they become immobile at the surface and do not desorb from the surface. Due to need of such behaviour in solid catalyst, transition metals are normally better catalyst (specially metals of group 7 to 9.)



(ii) **Selectivity** : Sometimes, the change in catalyst may change the reaction product. The selectivity of a catalyst is its ability to direct a reaction to yield a particular product. For example,



Can you predict the reason behind different action of different catalyst?

### SHAPE-SELECTIVE CATALYSIS BY ZEOLITES:

The catalytic reaction that depends upon the pore structure of the catalyst and the size of the reactant and product molecules is called shape-selective catalysis.

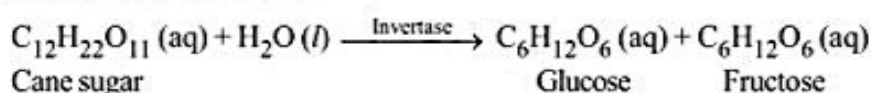
Zeolites are good shape-selective catalysts because of their honey comb-like structures. They are microporous aluminosilicates of general formula,  $M_{x/n} [\text{AlO}_2]_x \cdot [\text{SiO}_2]_m \cdot n\text{H}_2\text{O}$ , with three dimensional network of silicates in which some silicon atoms are replaced by aluminium atoms giving Al–O–Si framework. They are found in nature as well as synthesised for catalytic selectivity. Zeolites, before using as catalysts, are heated in vacuum. When the trapped water molecules come out, zeolite becomes porous, i.e., the cavities in the cage-like structure, which were occupied by water molecules, becomes vacant. The size of the pores generally varies between 260 pm to 740 pm. Thus, only those molecules can be adsorbed in these pores whose size is small enough to enter these cavities and also leave easily. Zeolites are being very widely used as catalysts in petrochemical industries for cracking of hydrocarbons and isomerisation. An important zeolite catalyst used in petroleum industry is ZSM-5, which converts alcohol directly into gasoline (petrol) by dehydrating them to give a mixture of hydrocarbons.

### ENZYME CATALYSIS:

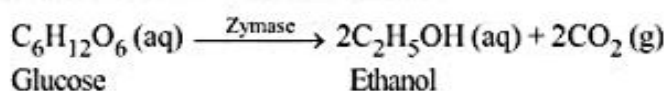
Enzymes are complex nitrogenous organic compounds which are produced by living plants and animals. They are protein molecules of high molecular masses (ranging from 15000 to 1000000 gm/mol) and form colloidal solutions in water.

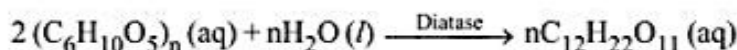
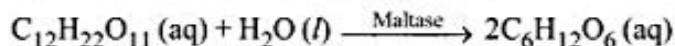
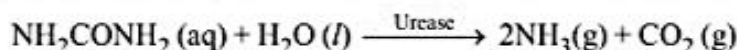
Enzymes are incredibly efficient catalysts. They catalyse large number of reactions, especially the natural processes. Most of the reactions occurring in the bodies of animals and plants to maintain the life process are catalysed by enzymes. This is why, enzymes are also called **biochemical catalysts** and the phenomenon is known as **biochemical catalysis**. Some of the enzyme catalysed reactions are:

#### (i) Inversion of cane sugar :



#### (ii) Conversion of glucose into ethanol:



**(iii) Conversion of starch into maltose :****(iv) Conversion of Maltose into Glucose:****(v) Decomposition of urea into ammonia and carbon dioxide :****(vi) Conversion of milk into curd :**

The enzyme lactobacilli helps in the conversion of milk into curd.

**CHARACTERISTICS OF ENZYME CATALYSIS:**

**(i) Most highly efficient :** One molecule of an enzyme may transform million molecules of the reactant into product, per minute.

**(ii) Highly specific nature :** Each enzyme is specific for a given reaction, i.e., one catalyst cannot catalyse more than one reaction. For example the enzyme urease catalyses the hydrolysis of urea only.

**(iii) Highly active at optimum temperature :** The rate of an enzyme catalysed reaction becomes maximum at a certain temperature called **optimum temperature**. For most of the enzyme, the optimum temperature is 298-310K.



**Can you predict whether our body temperature is suitable for the maximum catalytic activity of enzymes or not?**

**(iv) Highly active at optimum pH :** The rate of an enzyme catalysed reaction becomes maximum at a particular pH, called optimum pH. For most of the enzyme, the optimum pH is 5-7.

**(v) Influence of activators and coenzymes :** It is observed that when a small non-protein (vitamin) is present with an enzyme, the catalytic activity of enzyme enhances considerably. Such substances are called co-enzymes.

Similarly, the metal ions like  $Na^+$ ,  $Mn^{2+}$ ,  $Co^{2+}$ ,  $Cu^{2+}$  etc, when weakly bonded to enzyme molecules, increases the catalytic activity of enzymes. These metal ions are called activators.

**(vi) Influence of inhibitors and poisons :** The inhibitors or poisons interact with the active functional groups on the enzyme surface and often reduce or completely destroy the catalytic activity of the enzymes.

**MECHANISM OF ENZYME CATALYSIS :** There are a large number of cavities present at the surface of colloidal particles of enzymes. These cavities are of characteristic shape and possess active groups such as  $-NH_2$ ,  $-COOH$ ,  $-OH$ , etc. The molecules of the reactant (substrate), which have complementary shape, fit into these cavities just like a key fits into a lock. Due to the presence of active groups on the surface of catalyst, an activated complex is first formed, which then, decomposes to yield the products and enzyme molecules.

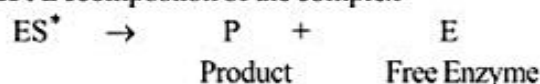


Such mechanism (key and lock model) was first proposed in 1913, by the biochemists Michaelis and Menten. It may be expressed kinetically as :

**Step- I :** Formation of enzyme - substrate complex :



**Step - II :** Decomposition of the complex



### CATALYSTS IN INDUSTRY :

Some of the important processes and their catalyst are given in below.

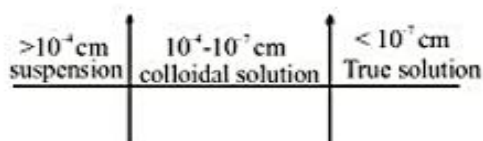
<i>Industrial process</i>	<i>Catalyst used</i>
Preparation of $\text{O}_2$ from $\text{KClO}_3$ (Hetero)	$\text{MnO}_2$
Haber's process for ammonia (Hetero)	Fe: Mo as promoter
Ostwald's process for $\text{HNO}_3$ from $\text{NH}_3$ (Hetero)	Pt Gauge
Chamber process for $\text{H}_2\text{SO}_4$ (Hetero)	Nitric oxide (NO) gas
Contact process for $\text{H}_2\text{SO}_4$ (Hetero)	$\text{V}_2\text{O}_5$
Deacon's process for manufacture of $\text{Cl}_2$ (Hetero)	$\text{CuCl}_2$
Bosch process for $\text{H}_2$ (Hetero)	$\text{Fe}_2\text{O}_3 + \text{Cr}_2\text{O}_3$
Manufacture of vegetable ghee (Hetero)	Ni, Cu as promoter
Hydrolysis of ester (Homo)	aq $\text{H}_2\text{SO}_4$
Cracking of hydrocarbon (Hetero)	Zeolites

## COLLOIDS

Graham classified substances into crystalloids and colloids, but this classification is not totally valid now as many crystalloids under certain conditions behave as colloids.

A colloidal state of matter may be defined as a state in which the size of the particles is such that they can pass through filter paper but not through a vegetable or animal membrane.

### Particle size



### Phase of colloids :

A colloidal system is heterogeneous in character. It consists of two phases, namely a dispersed phase and a dispersion medium.

- Dispersed Phase :** It is the component present in small proportion and is just like a solute in a true solution. For example, in the colloidal state of sulphur in water, the former acts as a dispersed phase.
- Dispersion Medium :** It is normally the component present in excess and is just like a solvent in a solution.

The particles of the dispersed phase are scattered in the dispersion medium in a colloidal system.

### Classification of colloids :

Colloids can be classified in a number of ways based upon some of their important characteristics.

(1) **Physical state of Dispersed Phase & Dispersion Medium:**

Depending upon whether the dispersed phase and the dispersion medium are solids, liquids or gaseous, eight types of colloidal system are possible. A gas mixed with another gas forms a homogeneous mixture and not a colloidal system. Typical examples of various type along with their characteristic names are given in table.

### COMMON COLLOIDAL SYSTEM

Dispersed Phase	Dispersion medium	Colloidal system	Examples
Gas	Liquid	Foam or froth	Soap sols, lemonade froth, whipped cream.
Gas	Solid	Solid foam	Pumice stone, styrene, foam, foam rubber.
Liquid	Gas	Aerosols of Liquids	Fog, clouds, fine insecticide sprays.
Liquid	Liquid	Emulsions	Milk
Liquid	Solid	Gels	Cheese, butter, boot polish, table jellies, curd.
Solid	Gas	Aerosols of Solid	Smoke, dust
Solid	Liquid	Sols	Must paint, starch dispersed in water, gold sol, muddy water, inks.
Solid	Solid	Solid sols	Ruby glass, some gem stones.





A colloidal system in which the dispersion medium is a liquid or gas are called sols. They are called hydrosols or aqua sols, if the dispersion medium is water. When the dispersion medium is alcohol or benzene, they are accordingly called alcohols or benzosol.

Colloidal systems in which the dispersion medium is a gas are called aerosols.



Solutions can be classified into 9 types where as colloids can be classified into 8 can you predict the reason?

Colloids in which the dispersion medium is a solid are called gels, e.g. cheese etc. They have a more rigid structure. Some colloids, such as gelatin, can behave both as a sol and a gel. At high temperature and low concentration of gelatin, the colloid is a hydrosol. But at low temperature and high gelatin concentration, the hydrosol can change into a gel.

- (2) **Based on interaction or affinity of phases :** On the basis of the affinity or interaction between the dispersed phase and the dispersion medium, the colloids may be classified into two types :
- (i) **Lyophilic Colloids :** The colloidal system in which the particle of dispersed phase have great affinity for the dispersion medium, are called lyophilic (solvent-loving) colloids. In such colloids, the dispersed phase does not get easily precipitated and the sols are more stable. Such colloidal systems, even if precipitated, may be reconverted to the colloidal state by simply agitating them with the dispersion medium. Hence lyophilic colloids are reversible. When the dispersion medium is water, these are called hydrophilic colloids. Some common examples of lyophilic colloids are gum, gelatin, starch, rubber, proteins, etc.
  - (ii) **Lyophobic colloids :** The colloidal system in which the dispersed phase have no affinity for the dispersion medium are called lyophobic (solvent hating) colloids. They are easily precipitated (or coagulated) on the addition of small amounts of the electrolyte, by heating or by shaking. They are less stable and irreversible. When the dispersion medium is water, these are known as hydrophobic colloids. Examples of lyophobic colloids include sols of metals and their insoluble compounds like sulphides and oxides.



The essential differences between the lyophilic and lyophobic colloids are summarised in table.

## DIFFERENCE BETWEEN LYOPHILIC AND LYOPHOBIC SOLS

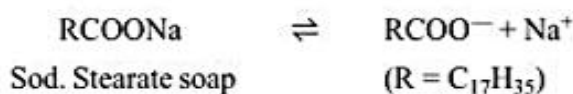
	<i>Property</i>	<i>Lyophilic sols</i>	<i>Lyophobic sols</i>
1.	Nature	Reversible	Irreversible
2.	Preparation	They are prepared very easily by shaking or warming the substance with dispersion medium. They do not required any electrolyte for stabilization.	They are difficult to prepare, Special methods are used. Addition of stabiliser is essential for their stability.
3.	Stability	They are very stable and are not easily coagulated by electrolytes.	They are generally unstable and get easily coagulated on addition of electrolytes.
4.	Charge	Particles carry no or very little charge depending upon the pH of the medium.	Colloidal particles have characteristic charge (positive or negative)
5.	Viscosity	Viscosity is much higher than that of the medium.	Viscosity is nearly the same as that of the medium
6.	Surface Tension that	Surface tension is usually less than of the medium.	Surface tension is nearly the same as that of the medium.
7.	Migration in electric field	The particles may or may not migrate in an electric field.	The colloidal particles migrate either towards cathode or anode in an electric field.
8.	Solvation	Particles are heavily solvated.	Particles are not solvated.
9.	Visibility seen	The particles cannot be seen under ultra microscope.	The particles though invisible, can be under ultra microscope.
10.	Tyndall effect	Less distinct.	More distinct.
11.	Action of electrolyte	Large amount of electrolyte is required to cause coagulation.	Small amount of electrolyte is sufficient to cause coagulation.
12.	Examples	Mostly organic substances e.g. starch, gums, proteins, gelatin etc.	Generally inorganic substance e.g., metal sols, sulphides and oxides sols.

(3) **Based on type of particles of the dispersed phase :** Depending upon the molecular size, the colloidal system has been classified into three classes :

(i) **Multimolecular colloids :** The multimolecular colloidal particles consists of aggregate of atoms of small molecules with diameters less than  $10^{-9}$  m or 1 nm.  
For example, a sol. of gold contains particles of various sizes having several atoms. A sol. of sulphur consists of particles containing a thousand or so  $S_2$  molecules. These particles are held together by vander Waal's forces. These are usually lyophobic sols.



- (ii) **Macromolecular colloids :** The macromolecular colloidal particles themselves are large molecules. They have very high molecular weights varying from thousands to millions. These substances are generally polymers. Naturally occurring macromolecules are such as starch, cellulose and proteins. Artificial macromolecules are such as polyethylene, nylon, polystyrene, dacron, synthetic rubber, plastics, etc. The size of these molecules are comparable to those of colloidal particles and therefore, their dispersion known as macromolecular colloids. Their dispersion also resemble true solutions in some respects.
- (iii) **The associated colloids or micelles :** These colloids behave as normal electrolytes at low concentrations but colloids at higher concentrations. This is because at higher concentrations, they form aggregated (associated) particles called micelles. Soap and synthetic detergents are examples of associated colloids. They furnish ions which may have colloidal dimensions.



The long-chain  $\text{RCOO}^-$  ions associates or aggregate at higher concentrations and form micelles and behave as colloids. They may contain 100 or more molecules.

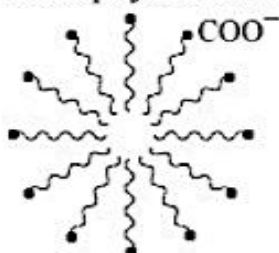
Sodium stearate  $\text{C}_{17}\text{H}_{35}\text{COONa}$  is an example of an associated colloid. In water it gives  $\text{Na}^+$  and stearate,  $\text{C}_{17}\text{H}_{35}\text{COO}^-$  ions. These ions associate to form micelles of colloidal size.



Colloids which behave as normal electrolytes at low concentration, but exhibit colloidal properties at higher concentration due to the formation of aggregated particles called micelles are referred to as associated colloids. The micelles are formed by the association of dispersed particles above a certain concentration and certain minimum concentration is required for the process of aggregation to take place. The minimum concentration required for micelle formation is called micellisation concentration (CMC) and its value depends upon the nature of the dispersed phase. For soaps CMC is  $10^{-3} \text{ mole L}^{-1}$ .

#### **Mechanism of Micelle Formation :**

Micelles are formed by surface active molecules called surfactants such as soaps and detergents. These molecules have lyophilic group at one end and a lyophobic group at the other end. Let us take the example of a soap (say sodium oleate,  $\text{C}_{17}\text{H}_{33}\text{COO}^-\text{Na}^+$ ). The long hydrocarbon part of oleate radical ( $\text{C}_{17}\text{H}_{33}-$ ) is lyophobic end while  $\text{COO}^-$  part is lyophilic end. When the concentration of the solution is below its CMC, sodium oleate behaves as a normal electrolyte and ionises to give  $\text{C}_{17}\text{H}_{33}\text{COO}^-$  and  $\text{Na}^+$  ions. When the concentration exceeds CMC, the lyophobic part starts receding away from the solvent and tends to approach each other. However, the polar  $\text{COO}^-$  ends tends to interact with the solvent (water). This finally leads to the formation of bigger molecules having the dimensions of colloidal particles. Thus 100 or more oleate ions are grouped together in a spherical way keeping their hydrocarbon parts inside and the  $-\text{COO}^-$  part remains projected in water.



## LIST OF SURFACTANTS AND THEIR CRITICAL MICELLE CONCENTRATION (CMC)

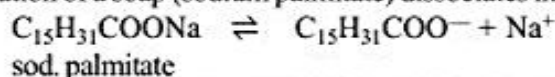
Surfactant	CMC (g/l)	Temp.(°C)
<i>Anionic</i>		
$\text{CH}_3(\text{CH}_2)_6\text{COONa}$	$6.5 \times 10^1$	20
$\text{CH}_3(\text{CH}_2)_{10}\text{COONa}$	5.6	20–70
$\text{CH}_3(\text{CH}_2)_7\text{OSO}_3\text{Na}$	$3.0 \times 10^1$	25–50
$\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3\text{Na}$	2.6	25–60
$\text{CH}_3(\text{CH}_2)_5\text{C}_6\text{H}_4\text{SO}_3\text{Na}$	9.8	75
$\text{CH}_3(\text{CH}_2)_{11}\text{C}_6\text{H}_4\text{SO}_3\text{Na}$	$4.0 \times 10^{-1}$	50–75
<i>Cationic</i>		
$\text{CH}_3(\text{CH}_2)_9\text{NH}_2\cdot\text{HCl}$	8.5	25
$\text{CH}_3(\text{CH}_2)_{11}\text{NH}_2\text{HCl}$	2.7	30–50
$\text{CH}_3(\text{CH}_2)_7\text{N}(\text{CH}_3)_3\text{Br}$	$7.8 \times 10^1$	25
$\text{CH}_3(\text{CH}_2)_{11}\text{N}(\text{CH}_3)_3\text{Br}$	5.4	25
<i>Non-ionic</i>		
$\text{CH}_3(\text{CH}_2)_7\text{C}_6\text{H}_{11}\text{O}_6$	7.3	25
$\text{C}_{12}\text{H}_{20}\text{O}_9(\text{C}_{16}\text{H}_{31}\text{O}_2)_2$	$1.1. \times 10^{-2}$	20
$\text{CH}_3(\text{CH}_2)_{10}\text{COOC}_{12}\text{H}_{21}\text{O}_{10}$	$7.1 \times 10^{-3}$	50



Can you observe some trend in CMC value.

**Origin of charge :** Various reasons have been given regarding the original of charge on the colloidal particles. These are given below :

- (i) **Frictional electrification :** It is believed to be frictional due to the rubbing of the dispersed phase particles with medium molecules.
- (ii) **Dissociation of the surface molecules :** It leads to electric charge on colloidal particles. For example, an aqueous solution of a soap (sodium palmitate) dissociates into ions.



The  $\text{Na}^+$  ions pass into the solution while  $\text{C}_{15}\text{H}_{31}\text{COO}^-$  ions have a tendency to form aggregates due to weak attractive forces present in the hydrocarbon chains. Thus, the anions which are of colloidal size bear negative charge.

- (iii) **Preferential adsorption of ions from solution :** The charge on the colloidal particles is generally acquired by preferentially adsorbing positive or negative ions from the electrolyte. Thus  $\text{AgCl}$  particles can adsorb  $\text{Cl}^-$  ions from chloride solutions and  $\text{Ag}^+$  ions from excess  $\text{Ag}^+$  ions solutions; the sol. will be negatively charged in the first case and positively charged in the second case.
- (iv) **Capture of electron :** It is from air during preparation of sol. by Bredig's arc method.



- (v) **Dissociation of molecular electrolytes on the surface of particles :**  $\text{H}_2\text{S}$  molecules get adsorbed on sulphides during precipitation. By dissociation of  $\text{H}_2\text{S}$ ,  $\text{H}^+$  ions are lost and colloidal particles become negatively charged.

### Electrical charged sols

S.No.	Positively charged sols	Negatively charged sols
1.	Ferric hydroxide, aluminium hydroxide	Metals such as Pt, Au, Ag, Metals sulphides, e.g. arsenious sulphide.
2.	Basic dyes such as methylene blue	Starch, clay, silicic acid.
3.	Haemoglobin	Acid dyes, such as eosin.

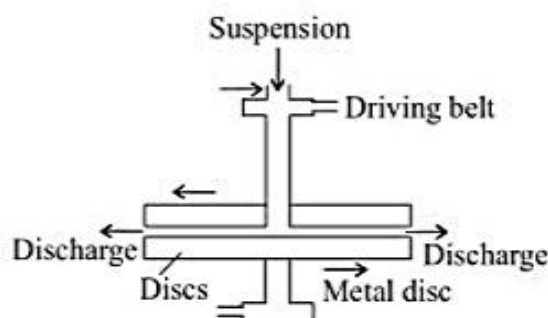
### Preparation of colloidal solutions

- (1) **Preparation of lyophilic sols :** The colloidal solutions of lyophilic colloids like starch, glue, gelatin etc., can be readily prepared by dissolving these substances in water either in cold or on warming. Solutions of colloidal electrolytes such as soaps and dye stuffs can also be prepared similarly.
- (2) **Preparation of lyophobic sols :** To get a substance in colloidal form either the substance in bulk is broken down into fine particles of colloidal dimension ( $1\text{\AA}$  to  $10^3\text{\AA}$ ) or increasing the size of molecular particles as to form larger aggregates. In some cases, a third substance is usually added to increase the stability of the sol. These substances are called stabilizers. Thus, there are two ways by which the lyophobic sols can be prepared :
  - (i) **Dispersion methods :** By splitting coarse aggregates of a substance into colloidal size.
  - (ii) **Condensation methods :** By aggregating very small particles (atoms, ions or molecules) into colloidal size.

S. No.	Dispersion methods	Condensation methods
1.	Mechanical dispersion	Exchange of solvents
2.	Electro-dispersion	Change of physical state
3.	Ultrasonic dispersion	Chemical methods : (i) Double decomposition (ii) Oxidation (iii) Reduction (iv) Hydrolysis

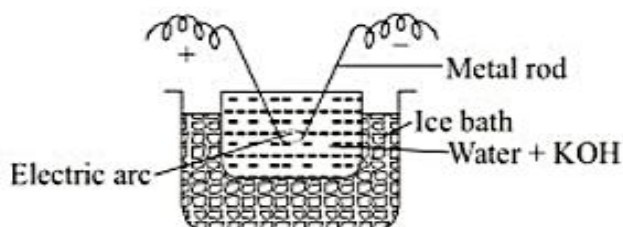
### Dispersion Methods

- (1) **Mechanical dispersion :** Solid material is first finely ground by usual methods. It is then mixed with dispersion medium which gives a coarse suspension. The suspension is now introduced into the colloid mill. The simplest form of colloid mill consists of two metal discs held at a small distance apart from one another and capable of revolving at a very high speed (about 7000 revolutions per minute) in opposite directions. The particles are ground down to colloidal size and are then dispersed in the liquid. A stabilizer is often added to stabilize the colloidal solution. Colloidal graphite (a lubricant) and printing ink



are made by this method. Tannin is used as a stabilizer in the preparation of colloidal graphite and gum arabic in lamp black colloidal solution (Indian ink).

- (2) **Electro-dispersion (Bredig's arc method) :** This method is suitable for the preparation of colloidal solutions of metals like gold, silver, platinum, etc. An arc is struck between the metal electrodes under the surface of water containing some stabilizing agents such as a trace of KOH. The water is cooled by immersing the



container in an ice bath. The intense heat of the arc vaporises some of the metal which condenses under cold water.

**Note :** (1) This method is not suitable when the dispersion medium is an organic liquid as considerable charring occurs.

(2) This method comprises both dispersion and condensation.

- (3) **Ultrasonic dispersion :** The sound waves of high frequency are usually called ultrasonic waves. These waves can be produced when quartz crystal discs are connected with a high frequency generator. The application of ultrasonic waves for the preparation of colloidal solutions was first introduced by Wood and Loomis, in 1927. Various substances like oils, mercury, sulphur, sulphides and oxides of metals can be dispersed into colloidal state very easily with the help of ultrasonic waves.

- (4) **Peptization :** The dispersion of a freshly precipitated material into colloidal solution by the action of an electrolyte in solution is termed peptization. The electrolyte used is called a peptizing agent.

A few examples of sols obtained by peptization are :

- (i) Freshly prepared ferric hydroxide on treatment with a small amount of ferric chloride solution at once forms a dark reddish brown solution. Ferric chloride acts as a peptizing agent.
- (ii) Freshly prepared stannic oxide on treatment with a small amount of dilute hydrochloric acid forms a stable colloidal solution of stannic oxide.
- (iii) Freshly precipitated silver chloride can be converted into a colloidal solution by a small amount of hydrochloric acid.
- (iv) Cadmium sulphide can be peptized with the help of hydrogen sulphide.



The process of peptization thus involves the adsorption of suitable ions (supplied by the electrolyte added—particularly a common ion) and electrically charged particles then split from the precipitate as colloidal particles.

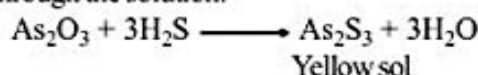
### Condensation Methods

(1) **By exchange of solvents :** If a solution of sulphur or phosphorus prepared in alcohol is poured into water, a colloidal solution of sulphur or phosphorus is obtained due to low solubility of sulphur or phosphorus in water. Thus, there are a number of substances whose colloidal solutions can be prepared by taking a solution of the substance in one solvent and pouring it into another solvent in which the substance is relatively less soluble.

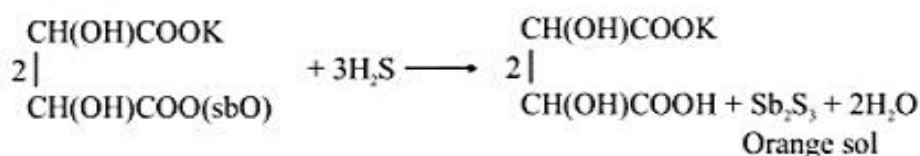
(2) **By change of physical state :** Colloidal solutions of certain elements such as mercury and sulphur are obtained by passing their vapour through cold water containing a stabilizer (an ammonium salt or a citrate)

(3) **Chemical methods :** The chemical methods involve chemical reactions in a medium in which the dispersed phase is sparingly soluble. A condition of supersaturation is produced but the actual precipitation is avoided. Some familiar reactions used are :

(a) **Double decomposition :** (i) Arsenious sulphide sol : A 1% solution of arsenious oxide is prepared in hot water. The solution is cooled, filtered and is then gradually in hot water saturated with hydrogen sulphide. This is continued till an intense yellow-coloured solution is obtained. Excess of  $\text{H}_2\text{S}$  is removed by bubbling hydrogen through the solution.



(ii) Antimony sulphide sol : A 0.5% solution of potassium antimonyl tartarate is added drop by drop to water saturated with  $\text{H}_2\text{S}$ , while  $\text{H}_2\text{S}$  is being passed through the solution. Orange coloured solution of antimony sulphide is obtained.



(b) **Oxidation :** A colloidal solution of sulphur is obtained by passing  $\text{H}_2\text{O}$  into a solution of sulphur dioxide.

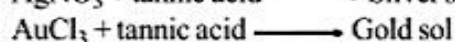
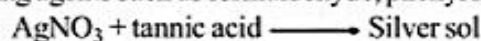


Sulphur sol can also be obtained when  $\text{H}_2\text{S}$  is bubbled through an oxidising agent (bromine water or nitric acid).

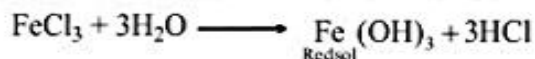
(c) **Reduction :** Colloidal solutions of metals like gold, silver, platinum, lead, etc., can be obtained when their salts solutions are acted upon by reducing agents.



Organic reducing agents such as formaldehyde, phenyl hydrazine, tannic acid, etc., can also be used.



(d) **Hydrolysis** : Colloidal solutions of some salts can be prepared by hydrolysis. A colloidal solution of ferric hydroxide is obtained by boiling a dilute solution of ferric chloride.]

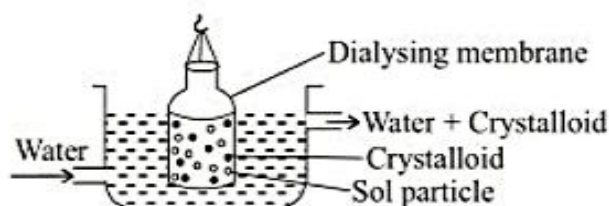


The colloidal solution of silicic acid is also obtained by hydrolysis of dilute solution of sodium silicate with 4N hydrochloric acid which is added drop by drop with constant stirring.

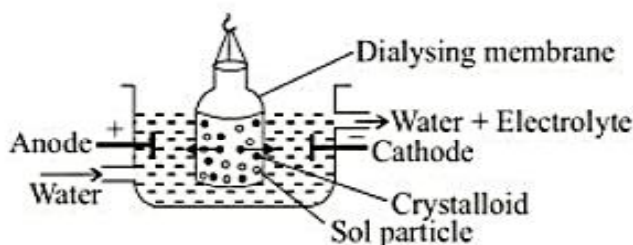
### Purification of Colloidal Solution

Colloidal solutions prepared by above methods generally contain excessive amount of electrolytes and some other soluble impurities. The presence of traces of electrolyte is essential for the stability of the colloidal solution but larger quantities coagulate it. It is, therefore, necessary to reduce the concentration of these soluble impurities to a requisite minimum. The process used for reducing of these impurities to a requisite minimum is known as purification of colloidal solution. The purification of colloidal solution is carried out by the following methods.

- (i) **Dialysis\*** : It is a process of removing a dissolved substance from a colloidal solution by means of diffusion through suitable membrane. Since, particles in true solution (ions or smaller molecules) can pass through animal membranes (bladder) or parchment paper or cellophane sheet but colloidal particles do not, the above can be used for dialysis. The apparatus used for this purpose is called dialyser. A bag of suitable membrane containing the colloidal solution is suspended in a vessel through which fresh water is continuously flown figure. The molecules and ions diffuse through the membrane into the outer water and pure colloidal solution is left behind.



- (ii) **Electro-dialysis** : Ordinarily, the process of dialysis is quite slow. It can be made faster by applying an electric field if the dissolved substance in the impure colloidal solution is only electrolyte. The process is then named electro-dialysis. The colloidal solution is placed between two electrodes while pure water is taken in a compartment on each side. Electrodes are fitted in the compartment as shown in figure the ions present in the colloidal solution migrate out to the oppositely charged electrodes.



- (iii) **Ultrafiltration** : Ultrafiltration is the process of separating the colloidal particles from the solvent and soluble solutes present in the colloidal solution by especially prepared filters, which are permeable to all substances except the colloidal particles.



Colloidal particles can pass through ordinary filter paper because the pores are too large. However, the pores of filter paper can be reduced in size by impregnating with collodion solution and subsequently hardened by soaking in formaldehyde. The usual collodion is a 4% solution of nitro-cellulose in a mixture of alcohol and ether. An ultrafilter paper may be prepared by soaking the filter paper in a collodion solution and hardened by formaldehyde and finally drying it. Thus, by using ultrafilter paper, the colloidal particles are separated from rest of the materials. Ultrafiltration is a slow process. To speed up the process, pressure or suction is used.

The colloidal particles left on the ultrafilter paper are then stirred with fresh dispersion medium (solvent) to get a pure colloidal solution.

### Properties of Colloidal Solutions :

#### (1) *Physical properties :*

(i) **Heterogeneity** : Colloidal solutions are heterogeneous in nature consisting of two phases viz, the dispersed phase and the dispersion medium. Experiments like dialysis and ultra filtration clearly indicate the heterogeneous character of colloidal system. Recent investigations however, shown that colloidal solutions are neither obviously homogeneous nor obviously heterogeneous.

(ii) **Filterability** : Colloidal particles readily pass through ordinary filter papers. It is because the size of the pores of the filter paper is larger than that of the colloidal particles.

(iii) **Non-settling nature** : Colloidal solutions are quite stable as the colloidal particles remain suspended in the dispersion medium indefinitely. Thus there is no effect of gravity on the colloidal particles.

(iv) **Colour** : The colour of the colloidal solution is not always the same as the colour of the substances in the bulk. The colour of the colloidal solution depends upon the following factors :

- (a) Size and shape of colloidal particles.
- (b) Wavelength of the source of light.
- (c) Method of preparation of the colloidal solution.
- (d) Nature of the colloidal solution.
- (e) The way an observer receives the light, i.e., whether by reflection or by transmission.
- (f) **Stability** : Colloidal solutions are quite stable. Only a few solutions of larger particles may settle but very slowly.

#### Examples :

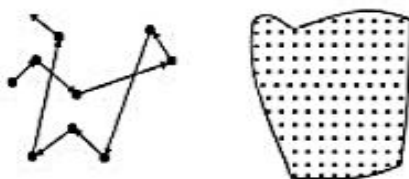
- (i) Finest gold is red in colour. As the size of particles increases, it becomes purple.
- (ii) Dilute milk gives a bluish tinge in reflected light whereas reddish tinge in transmitted light.

#### (2) *Mechanical Properties :*

(a) **Brownian movement** : Colloids particles exhibit a ceaseless random and swarming motion. This kinetic activity of particles suspended in the liquid is called Brownina movement. Robert Brown first observed this motion with pollen grains suspended in water.

**Cause of movement** : Brownian movement is due to bombardment of the dispersed particles by molecules of the medium. The Brownian movement (figure) depends upon the size of sol. particles. With the increase in the size of the particle, the chance of unequal bombardment decrease, and the Brownial movement too disappears. It is due to the fact that the suspension fails to exhibit this phe-nomenon.

It should be noted that Brownian movement does not change with time but changes with temperatures.

**Importance :**

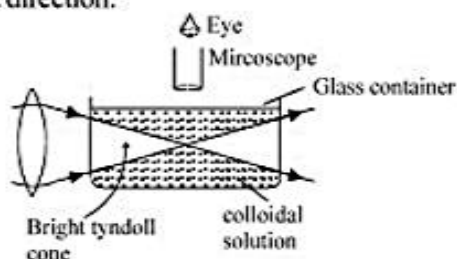
- (i) Brownian movement is a direct demonstration of the assumption that the molecules in a gas or solution are in a state of constant ceaseless motion. Thus it confirms kinetic theory.
- (ii) Brownian movement does not allow the colloidal particles to settle down due to gravity and thus is responsible for their stability.
- (iii) Brownian movement helps to calculate the Avogadro's number (Detail beyond the scope of the book).

**(b) Sedimentation :** Heavier sol. particle tend to settle down very slowly under the influence of gravity. This phenomenon is called sedimentation.

**(3) Optical Properties (Tyndal Effect) :**

When a strong and converging beam of light is passed through a colloidal solution, its path becomes visible (bluish light) when viewed at right angles to the beam of light (figure). This effect is called Tyndall effect. The light is observed as a bluish cone which is called Tyndall cone.

The Tyndall effect is due to scattering of light by the colloidal particles. The scattering of light cannot be due to simple reflection, because the size of the particles is smaller than the wave, length of the visible light and they are unable to reflect light waves. In fact, colloidal particles first absorb light and then a part of the absorbed light is scattered from the surface of the colloidal particles as a light of shorter wavelength. Since maximum scattering of light takes place at right angles to the place of incident light, it becomes visible when seen from that direction.



The Tyndall effect is observed under the following conditions :

- (i) The diameter of the dispersed particles must not be much smaller than the wavelength of light employed.
- (ii) The refractive indices of the dispersed phase and the dispersion medium must differ widely. This condition is fulfilled by lyophobic colloids.

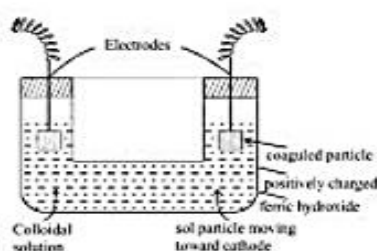
It is important to note that Tyndall effect is not shown by true solutions as their particles are too small to cause scattering. Tyndall effect has been used in devising ultramicroscope and in determining the number of colloidal particles in a colloidal solution.

**(4) Electrical Properties :** The two electrical properties of colloidal solutions are :

- (a) Electrophoresis or Cataphoresis and
- (b) Electro-osmosis

**(a) Electrophoresis or Cataphoresis :** In a colloidal solution, the colloidal particles are electrically charged and the dispersion medium has equal but opposite charge. Thus colloidal solution on the whole is electrically neutral. When an electric current is passed through a colloidal solution, the charged particles move towards the oppositely charged electrode where coagulate due to loss of charge.





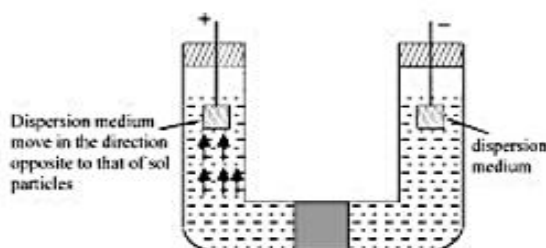
The phenomenon involving the migration of colloidal particles under the influence of electric field towards the oppositely charged electrode, is called electrophoresis or cataphoresis.

This phenomenon is used to determine the charge on the colloidal particles. For example, when a sol. of ferric hydroxide is taken in a U-tube and subjected to electric field, the ferric hydroxide (sol.) particles get accumulated near the cathode (figure). This shows that ferric hydroxide sol. particles are positively charged.

The sol. particles of metals and their sulphides are found to be negatively charged while those of metal hydroxides are positively charged. Basic dyes such as methylene blue haemoglobin are positively charged while acid dyes like are negatively charged.

**(b) Electro-osmosis :** The phenomenon involving the migration of the dispersion medium and not the colloidal particles under the influence of an electric field is electro-osmosis.

Take the pure solvent (dispersion medium) in two limbs of U-tube. In the lower middle portion of U-tube, a porous diaphragm containing the colloidal system is present which divides the U-tube in two sections. In each section of U-tube, an electrode is present, as shown in figure. When the electrode potential is applied to the electrodes, the solid phase of sol. (colloidal system) cannot move but the solvent (dispersion medium) moves through the porous diaphragm towards one of the electrodes. The direction of migration of dispersion medium due to electro-osmosis determines the charge on sol. particles e.g., if the dispersion medium moves towards the cathode (negative electrode), the sol. particles are also negatively charged because the dispersion medium is positively charged as on the whole colloidal solution is neutral.



**(c) Coagulation :** the colloidal sols are stable due to the presence of electric charges on the colloidal particles. Because of the electrical repulsion, the particles do not come close to one another to form precipitates. The removal of charge by any means will lead to the aggregation of particles and hence precipitation will occur immediately.

**This process by means of which the particles of the dispersed phase in a sol. are precipitated is known as coagulation.**

If the coagulated particles instead of settling at the bottom of the container, float on the surface of the dispersion medium, the coagulation is called *flocculation*.

Most of the sols are coagulated by adding an electrolyte of opposite sign. This is due to the fact that the colloidal particles take up the ions of electrolyte whose charges are opposite to that on colloidal particles with the result that charge on the colloidal particles is neutralized. Thus coagulation takes place. For example, arsenious sulphide sol. (negatively charged) precipitated by adding barium chloride solution. It is due to the fact that the negatively charged particles of the sol. take up barium ions and get neutralized which lower the stability. As a result precipitation takes place.

It is observed that different amounts of different electrolytes is required to bring coagulation of a particular solution.



The minimum amount of an electrolyte required to cause precipitation of one litre of a colloidal solution is called **coagulation value** or **flocculation value** of the electrolyte for the sol. The reciprocal of coagulation value is regarded as the **coagulating power**.

For example, the coagulation values of NaCl, BaCl<sub>2</sub> and AlCl<sub>3</sub> for arsenic sulphide sol. are 51, 0.69 and 0.093 millimoles/litre respectively. Thus their coagulating powers are  $\frac{1}{51}$ ,  $\frac{1}{0.69}$  and  $\frac{1}{0.093}$  i.e., 0.0196, 1.449 and 10.75 respectively.

The coagulation values of a few electrolytes for negatively charged arsenic sulphide and positively charged ferric hydroxide sol. are given in table given below. The valency of the coagulation ion (the ion whose charge is opposite to that of the colloidal particles) is also give.

### COAGULATION VALUES OF DIFFERENT ELECTROLYTES

Arsenic sulphide sol.			Ferric hydroxide sol.		
Electrolyte	Valency of coagulating cation	coagulation value (millimoles /litre)	Electrolyte	Valency of coagulating cation	coagulation value (millimoles/litre)
K <sub>2</sub> SO <sub>4</sub>	1	63	KBr	1	138
NaCl	1	51	KNO <sub>3</sub>	1	132
KNO <sub>3</sub>	1	50	KCl	1	103
MgSO <sub>4</sub>	2	0.81	K <sub>2</sub> CrO <sub>4</sub>	2	0.320
BaCl <sub>2</sub>	2	0.69	K <sub>2</sub> SO <sub>4</sub>	2	0.215
AlCl <sub>3</sub>	3	0.093	K <sub>3</sub> Fe(Cn) <sub>6</sub>	3	0.096

From the above table, it is clear that the coagulating power of Al<sup>3+</sup> ions in precipitating the arsenic sulphide sol. is approximately 550 times more than that of sodium (Na<sup>+</sup>) or potassium (K<sup>+</sup>) ions. Again, it is observed that the negatively charged arsenic sulphide sol. is coagulated by cations while positively charged ferric hydroxide sol. is coagulated by anions.

**Hardy-Schulz rules :** H. Schulze (1882) and W.B. Hardy (1900) suggested the following rules to discuss the effect of electrolytes of the coagulation of the sol.





- (1) Only the ions carrying charge opposite to the one present on the sol. particles are effective to cause coagulation, e.g., the negative charged sol. is best coagulated by cations and a positive sol. is coagulated by anions.
- (2) The charge on coagulating ion influences the coagulation of sol. In general, the coagulating power of the active ion increases with the valency of the active ion. After observing the regularities concerning the sign and valency of the active ion, a law was proposed by Hardy and Schulz which is termed as Hardy-Schulze law which is stated as follows:

**"Higher is the valency of the active ion, greater will be its power to precipitate the sol."**

Thus, coagulating power of cations is in the order of  $\text{Al}^{3+} > \text{Ba}^{2+}$  or  $\text{Mg}^{2+} > \text{Na}^+$  or  $\text{K}^+$ .

Similarly, to coagulating the positively charged sol. the coagulating power of anion is in the order of  $[\text{Fe}(\text{CN})_6]^{4-} > \text{PO}_4^{3-} > \text{SO}_4^{2-} > \text{Cl}^-$

#### **Some other methods of coagulation :**

Apart from the addition of electrolyte, coagulation can also be carried out by following methods:

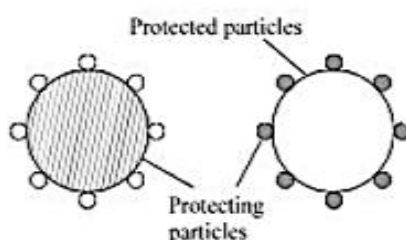
- (i) **By persistent dialysis :** It has been observed that traces of electrolytes are associated with the solution due to which it is stable. If the solution is subjected to prolonged dialysis, the traces of electrolytes are removed and coagulation takes place.
  - (ii) **By mutual coagulation of colloids :** When two sols of oppositely charges are mixed together in a suitable proportion, the coagulation takes place. The charge of one is neutralized by the other. For example, when negatively charged arsenic sulphide sol. is added to positively charged ferric hydroxide sol., the precipitation of both occurs simultaneously.
  - (iii) **By electrical method :** If the electrical charge of lyophobic sol. is removed by applying any electric field such as in electrophoresis, they also precipitate out.
  - (iv) By excessive cooling or by excessive heating.
- (5) **Colligative properties :** Colloidal solutions too exhibit colligative properties such as osmotic pressure, lowering of vapour pressure, depression in freezing point and elevation in boiling point. But the effect of colloidal particles on colligative properties except osmotic pressure is very small. This is due to the large size of colloidal particles. The number of colloidal particles produced by a given mass of colloid is much less than the number produced in a molecular solution, containing the same mass of solute. Hence the colligative effect in colloidal solutions is too less.

\*

#### **PROTECTIVE COLLOIDS :**

Lyophilic sols are more stable than the lyophobic sols. This is because, lyophilic colloids are extensively hydrated and these hydrated particles do not combine to form large aggregates.

Lyophobic sols are more easily coagulated by the addition of suitable electrolyte. To avoid the precipitation of lyophobic sol. by the addition of electrolyte, some lyophilic colloid is added to it. Such lyophilic colloid is called protective colloid and the action of lyophilic colloid by the electrolytes is known as protective anion. The substances commonly used as protective colloids are gelatin, albumin, gum arabic, casein, starch, glue etc. A gold sol. containing a little gelatin as protective colloid needs a very large amount of sodium chloride to coagulate the sol.



**Explanation :** The particles of the protective colloid get adsorbed on the particles of the lyophobic colloid, thereby forming a protective layer around it (figure). The protective layer prevents the precipitating ions from coming in contact with the colloidal particles.

According to a recent view, the increase in stability of the lyophobic colloid is due to the mutual adsorption of the lyophilic and lyophobic colloids. It is immaterial which is adsorbed on which. In fact the smaller particles, whether of the protective colloid or the lyophobic colloid, are adsorbed on the bigger particles.

Gold number of a protective colloid is a minimum weight of it in milligrams which must be added to 10 ml of a standard red gold sol so that no coagulation of the gold sol. (i.e. change of colour from red to blue) takes place when 1 ml of 10 % sodium chloride solution is rapidly added to it. Obviously, smaller the gold number of a protective colloid, the greater is the protective action.

#### **Isoelectric Point of Colloid :**

The hydrogen ion concentration at which the colloidal particles are neither positively charged nor negatively charged (i.e. uncharged) is known as isoelectric point of the colloid. At this point lyophilic colloid is expected to have minimum stability because at this point particles have no charge. The isoelectric point of gelatin is 4.7. This indicates that at pH = 4.7, gelatin has no electrophoretic motion. Below 4.7, it moves towards the cathode and above 4.7 it moves towards the anode. It is not always true, e.g., silicic acid has been found to have maximum stability at the isoelectric point.

#### **Electric double layer :**

The surface of a colloidal particle acquires a positive or a negative charge by selective adsorption of ions carrying +ve or -ve charges respectively. The charged layer attracts counter ions from the medium which forms a second layer. Thus, an electrical double layer is formed on the surface of the particles i.e., one due to adsorbed ions and the other due to oppositely charged ions forming a diffused layer. This layer consists of ions of both the signs, but its net charge is equal and opposite to those adsorbed by the colloidal particles. The existence of charges of opposite signs on the fixed and diffused parts of the double layer creates a potential between these layers. This potential difference between the fixed charge layer and diffused layer of opposite charge is called electrokinetic potential or zeta potential.

#### **Illustration**

1. For the coagulation of 100 ml of arsenious sulphide sol, 5 ml of 1 M NaCl is required. What is the flocculation value of NaCl?

**Sol.** 5 ml of 1 M NaCl contains  $\text{NaCl} = \frac{1}{1000} \times 5 \text{ moles} = 5 \text{ millimoles}$

Thus, 100 ml of  $\text{As}_2\text{S}_3$  sol require NaCl for complete coagulation = 5 millimoles

$\therefore$  1 L, i.e., 1000 ml of the sol require NaCl for complete coagulation = 50 millimoles

$\therefore$  By definition, flocculation value of NaCl = 50



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**Exercise**


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1. The coagulation of 100 mL of a colloidal sol of gold is completely prevented by addition of 0.25 g of starch to it before adding 10 mL of 10% NaCl solution. Find out the gold number of starch.

Ans. 25.

**Note that** to test 100 mL of gold sol, 10 mL of 10% NaCl solution is required as for 10 mL of gold sol, 1 mL of 10% NaCl solution is required.

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## EMULSIONS

An emulsion is a colloidal solution of a liquid. It may be defined as a heterogeneous system consisting of more than one immiscible liquids dispersed in one another in the form of droplets whose diameter, in general, exceeds  $0.1\ \mu$ .

For example, milk is an emulsion in which small drops of liquid fat are dispersed in aqueous medium. Cod liver oil is an emulsion in which the water drops are dispersed in the oil. This means in most of the emulsions one of the liquid is water and the other liquid is oil. Here the term 'oil' is used to represent all organic substances which are soluble in water.

The emulsion are classified as :

- (1) **Oil in water type emulsion (O/W):** In this emulsion, oil is the dispersed phase and water is the dispersion medium. It is denoted by O/W or O in W. For example, milk (liquid fat dispersed in water), vanishing cream, etc.
- (2) **Water in oil type :** In this emulsion, water is the dispersed phase and oil is the dispersion medium. It is denoted by W/O or W in O. For example, butter, cod liver oil, cold cream, etc.

The type of emulsion obtained by agitating two immiscible liquids depends upon the relative amounts of two components liquids. The liquid that is in excess forms the dispersion medium. Thus, the two types of emulsions can be interconverted into each other by changing the concentration of one of the liquids.

**Distinction between two types of emulsions :** the two types of emulsions may be distinguished from each other in a number of ways.

- (1) **Dye test :** It involves the addition of oil soluble dye to the emulsion under experiment. If the emulsion acquires the colour of the dye readily, it is water-in-oil type emulsion and if the emulsion remains colourless, it is oil-in-water type emulsion.
- (2) **Conductivity test :** It involves the addition of electrolyte to the emulsion under experiment. If the conductivity of the emulsion increases appreciably with the addition of electrolyte, it is oil-in-water type emulsion and if conductivity is very small, it is water-in-oil type emulsion.
- (3) **Dilution test :** As a general rule, an emulsion can be diluted with the dispersion medium while the addition of the dispersed phase forms a separate layer. Thus, if an emulsion can be diluted with oil, it is water-in-oil type.

**Preparation of emulsion (Emulsification) :** Emulsification is the process which involves the preparation of emulsion. Generally, an emulsion is prepared by subjecting a mixture of the immiscible liquid to a distinct layers upon standing. The oil globules rise to form an upper layer while aqueous medium forms lower layers. To prevent the separation of layers and to get the stable emulsion, a small quantity of the third substance is added. This substance which stabilizes the emulsion is called *emulsifier* or *emulsifying*

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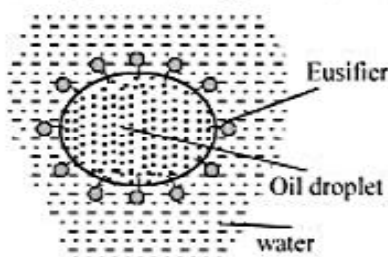
*agent*. The commonly used emulsifying agents are soaps, detergents and lyophilic colloids. Casein, a lyophilic colloid present in milk, acts as an emulsifier as it forms a protective layer around fat molecules dispersed in water. Hence milk is a fairly stable emulsion.

**Function of emulsifier :** The main function of emulsifier or emulsifying agents is to lower the interfacial tension between oil and water and thus helps the intermixing of two liquids. For example, a molecule of a soap or detergent (emulsifier) gets concentrated at the interface between oil and water. The polar end of the emulsifier is in water and non-polar end is in oil as shown in figure.

In a soap,  $\text{RCOONa}$ , R is the non-polar end, whereas  $\text{COO}^- \text{Na}^+$  is the polar end.

**Properties of emulsion :**

- (i) The size of particles of the dispersed phase of an emulsion is usually larger than in sols.
- (ii) Like colloidal particles, emulsions exhibit properties such as Tyndall effect, Brownian movement (provided the particles are not too large), electrophoresis, coagulation, etc.



**Demulsification :** The process which involves the breaking of an emulsion into two separate liquid layers is called demulsification. The following methods may be used to bring demulsification:

- (1) **Chemical Methods :** An emulsion may be demulsified by adding a chemical substance whose action on the dispersed phase and the dispersion medium is opposite to that of the original emulsifying agent used to produce the stable emulsion.
- (2) **Centrifugation :** Cream is separated from milk by the centrifugal method.
- (3) **Cooling :** Fat can be removed from milk by keeping it in a refrigerator for a few hours.

**Demulsification :**

Besides the above noted methods of demulsification, the following methods have also been developed :

- (i) Suitable centrifugal action-milk cream is separated from milk by centrifugation.
- (ii) Application of electric field-electrophoresis.
- (iii) Addition of an electrolyte having multivalent opposite charge than that on the dispersed phase.
- (iv) Chemical destruction of stabiliser.
- (v) Distilling off of one of the components, usually water.
- (vi) Addition of demulsifiers like alcohol, phenol etc.

**Oil in water type emulsion (O/W) Use of emulsion :**

- (1) Many pharmaceutical preparations-medicines, ointments, creams and various lotions are emulsions. It is believed that medicines are more effective and easily assimilated by the body tissues when they are in colloidal form i.e., emulsion.
- (2) All paints are emulsions.
- (3) The digestion of fat in the intestines is helped by emulsification. A little of the fat forms a medium soap (emulsifier) with the alkaline solution of the intestine and this soap emulsifies the rest of the fats, thus making it easier for the digestive enzymes to do their metabolic functions.



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- (4) Soaps and detergents remove dust and dirt from the dirty piece of cloth by making an oil in water emulsion.
  - (5) Milk is an emulsion of liquid fats in water.
  - (6) In the process of metallurgy, one of the important steps is the concentration of ore which is usually done by froth floatation process in which an oil is added to the finely-divided ore taken in water. The particles of ore go on the surface due to formation of foams while the other impurities are left at the bottom of the vessel.
  - (7) The emulsion of asphalt in water is used in road making and building.

### ***Illustration***

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**1. Answer the following :**

- (i) Explain demulsification.
- (ii) Can a colloidal solution conduct electricity ?
- (iii) What happens when gelatin is added to gold sol ?

- Sol.**
- (i) Breaking of an emulsion into constituent liquids
  - (ii) Yes
  - (iii) To increase stability
- 

### ***Exercise***

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**1. Classify the following into positively charged and negatively charged colloidal solutions.**

- (a) Ferric hydroxide
- (b) Arsenious sulphide
- (c) Gold
- (d) Stannic oxide

- Ans.**
- (a) Ferric hydroxide - positively charged
  - (b) Arsenious sulphide negatively charged
  - (c) Gold - negatively charged
  - (d) Stannic oxide-positively charged
- 

## ***GELS***

Colloidal system in which liquids are the dispersed phase and solid act as the dispersion medium are called gels. The common examples are : boot polishes, jelly, gum arabic, agar agar, processed cheese and silicic acid.

When the gels are allowed to stand for a long time, they give out small quantities of trapped liquids with accumulate on its surface. This action of gels is known as Synresis or Weeping. Some gels such as silica, gelatin and ferric hydroxide liquify on shaking and reset on allowing to stand. This phenomenon of Sol-gel transformation is called thixotropy.

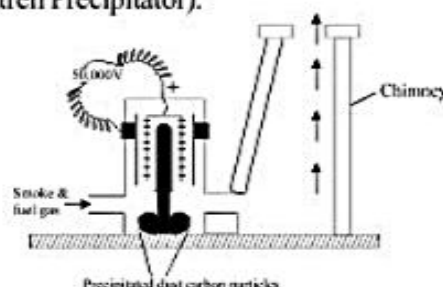
Gels are divided into two categories i.e. elastic gels and non elastic gels. The two categories differ from their behaviour towards dehydration and rehydration as under.

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S.No.	Elastic gels	Non-elastic gels
1.	They change to solid mass on dehydration which can be changed back to original form by addition of water followed by warming.	They change to solid mass on dehydration which cannot be changed back to original form with water.
2.	They absorb water when placed in it with simultaneous swelling. This phenomenon is called imbibation.	They do not exhibit imbibation.

### Uses of Colloids :

- (1) **Medicines :** The medicines containing gold, silver or calcium etc. in colloidal form are more effective and easily assimilated by the human systems.
- (2) **Dyes :** In dyeing, mordants colloidal substances are used in textile dyeing industry to fasten dyes.
- (3) **Rubber industry :** Latex is a colloidal solution of negatively charged particles. The article to be rubber plated is made the anode. Under the influence of electric field the rubber particles get deposited on the anode and the article gets rubber plated.
- (4) **Smoke screens :** Smoke screens which consist of titanium dioxide dispersed in air are used in warfare for the purpose of concealment and camouflage.
- (5) **Formation of delta :** The river water carries with it charged clay particles and many other substances in the form of colloidal solution. When the sea water comes in contact with these particles, the colloidal particles in river water are coagulated by the electrolytes present in sea water to form deltas.
- (6) **Purification of water :** The turbidity in water is due to the presence of negatively charged clay particles. The addition of potash alum, i.e.,  $\text{Al}^{3+}$  ions neutralizes the negative charge on the colloidal particles and thus causes their coagulation. The coagulated matter settles down and thus becomes clear.
- (7) **Artificial rain :** Artificial rain can be caused by throwing electrified sand on clouds which are colloidal solutions or charged particles of water in air.
- (8) **Smoke precipitation :** Smoke coming out of the chimney in industrial area is a nuisance and health hazard. It is a colloidal particles are charged particles and thus they are removed from fuel gases by electrical precipitation (Cottrell Precipitator).



In cottrell precipitator, the smoke is made to pass through chambers fitted with highly electrically charged plates which precipitate the carbon and dust particles leaving in the gases to escape through chimney (figure).

- (9) **Sewage disposal :** Sewage water consists of particles of dirt, rubbish, mud, etc., which are of colloidal dimensions and carry an electric charge and thus do not settle down easily. These particles can thus be removed by cataphoresis. A system of two tanks fitted with metallic electrodes is used for this purpose.



When electric field is created, then the dust particles are coagulated on the oppositely charged electrodes. The deposit may be utilized as a manure.

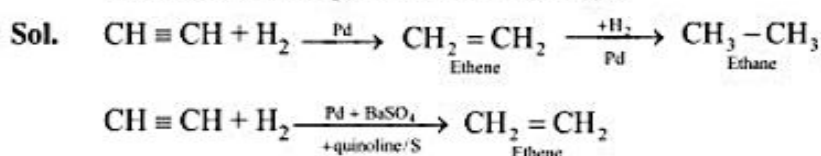
- (10) **Cleansing action of soap and detergent :** Soap solution may be used to wash off the dirt sticking to the fabric, in the presence  
 (i) If it forms a colloidal solution in water forms (micelles), removes dirt by simple adsorption of oily substance and thus washes away.  
 (ii) It decreases the interfacial tension between water and grease, and it causes the emulsification of grease in water. By mechanical action such as rubbing, the dirt particles are also detached along with the oily material.
- (11) **In Photography :** Various colloidal systems are used in photographic process. In the preparation of photographic plates, the silver bromide in gelatin is coated on thin glass plates. In developing and fixation, various colloidal substances are used. In different kinds of colour printing, gelatin and other colloidal mixtures are used.
- (12) **Blue colour of the sky :** Colloidal particles scatter only blue light and the rest of it is absorbed. In sky there are a number of dust and water particles. They scatter blue light and, therefore, sky looks bluish. If there were no scattering, the sky would have appeared totally dark.

### Illustration

1. Why the sun looks red at the time of setting ? Explain on the basis of colloidal properties.

**Sol.** At the time of setting, the sun is at the horizon. The light emitted by the sun has to travel a longer distance through the atmosphere. As a result, blue part of the light is scattered away by the dust particles in the atmosphere. Hence, the red part is visible.

2. Addition of  $H_2$  to acetylene gives ethane in presence of palladium but if  $BaSO_4$  and quinoline or sulphur are also added, the product is ethene. Why ?



$BaSO_4$  + quinoline/S poison the catalyst. Hence, the efficiency of the catalyst decreases and the reaction stops at the first stage of reduction.

3. Explain the following observations :

- (a) Ferric hydroxide sol gets coagulated on adding sodium chloride solution  
 (b) Cottrell's smoke precipitation is fitted at the mouth of the chimney used in factories  
 (c) Physical adsorption is multilayered while chemisorption is monolayered

**Sol.** (a) Ferric hydroxide is positively charged. It is coagulated by the oppositely charged chloride ( $Cl^-$ ) ions.  
 (b) Smoke is a colloidal dispersion containing charged carbon particles. Cottrell's precipitator attracts the charged carbon particles which are precipitated and hot air free of carbon particles escapes from the chimney.  
 (c) In physical adsorption, first layer is adsorbed on the adsorbent, second layer is adsorbed on the first layer and this continues. In chemisorption, there is reaction between adsorption and adsorbent forming a surface compound. The adsorbent is now covered and cannot react with more of adsorbate.



**Exercise**

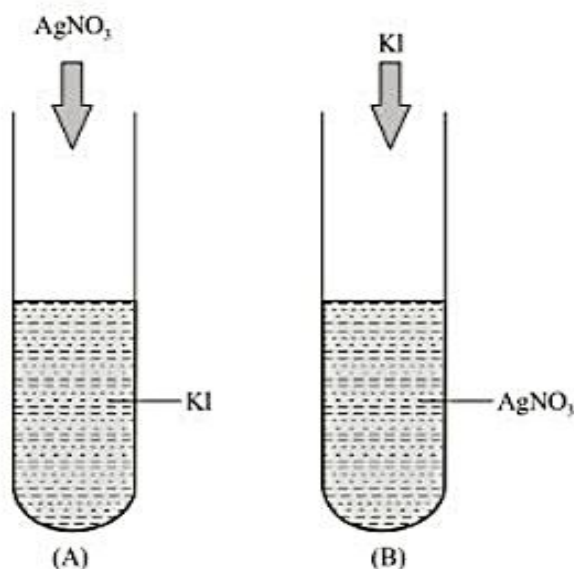
1. In an adsorption experiment, a graph between  $\log (x/m)$  versus  $\log P$  was found to be linear with a slope of  $45^\circ$ . The intercept on the  $\log (x/m)$  axis was found to be 0.3010. Calculate the amount of the gas adsorbed per gram of charcoal under a pressure of 0.5 atmosphere.

Ans. 1.0

2. The volume of nitrogen gas  $v_m$  (measured at STP) required to cover a sample of silica gel with a monomolecular layer is  $129 \text{ cm}^3 \text{ g}^{-1}$  of gel. Calculate the surface area per gram of the gel if each nitrogen molecule occupies  $16.2 \times 10^{-20} \text{ m}^2$ .

Ans.  $561.8 \text{ m}^2$ .

3. The colloidal solution of AgI is prepared by two different methods as shown in Fig.



(i) What is the charge on AgI colloidal particles in the two tubes (A) and (B) ?

(ii) Give reason for the origin of charge

- Ans. (i) In tube A, as  $\text{AgNO}_3$  is added in excess, the common  $\text{Ag}^+$  ions are adsorbed on AgI particles. Hence, charge on the colloidal particles is positive. In tube B, as KI is added in excess, common  $\text{I}^-$  ions are adsorbed on the colloidal particles and charge is negative.

(ii) Reason for origin of charge is the preferential adsorption of common ions of the electrolyte present in excess on the colloidal particles.

## SOLVED EXAMPLES

- Q.1** During adsorption, a substance  
 (A) accumulates on the surface of the other substance  
 (B) goes into the body of other substance  
 (C) remains close to other substance  
 (D) forms an aggregate with other substance
- Ans.** (A)
- Sol.** Adsorption is a surface phenomenon. The compound which is being adsorbed is known as 'adsorbate'. It concentrates on the surface of other compound known as 'adsorbent'.
- Q.2** Which of the following compounds would exhibit positive adsorption when dissolved in water?  
 (A) sodium sulphate (B) potassium nitrate (C) bathing soap (D) dyes
- Ans.** (C, D)
- Sol.** Among the compounds given above, bathing soap and dyes are capillary active substances, that is, these will rise and get concentrated at the surface of water. This is positive adsorption.
- Q.3** Sorption is the term used when  
 (A) adsorption takes place  
 (B) absorption takes place  
 (C) desorption takes place  
 (D) it is not possible to differentiate between adsorption and absorption
- Ans.** (D)
- Sol.** When it is not possible to differentiate between adsorption or absorption, the term 'sorption' is used.
- Q.4** Which of the following isotherms consider a multilayer formation?  
 (A) Langmuir (B) Freundlich (C) B.E.T (D) all of these
- Ans.** (C)
- Sol.** Only B.E.T considers a multilayer formation.
- Q.5**  $\text{As}_2\text{S}_3$  colloidal solution is obtained by  
 (A) treating a solution of  $\text{As}_2\text{O}_3$  with  $\text{Na}_2\text{S}$  (B) passing  $\text{H}_2\text{S}$  in a solution of  $\text{As}_2\text{O}_3$   
 (C) heating As and S. (D) reacting  $\text{As}_2\text{O}_3$  with  $\text{H}_2\text{SO}_4$  (dil.)
- Ans.** (B)
- Sol.**  $\text{As}_2\text{S}_3$  colloidal solution is prepared by passing  $\text{H}_2\text{S}$  in a solution of  $\text{As}_2\text{O}_3$ .  

$$\text{As}_2\text{O}_3 + 3\text{H}_2\text{S} \rightarrow \text{As}_2\text{S}_3 + 3\text{H}_2\text{O}$$
- Q.6** Which of the following does not give a colloidal solution of sulphur?  
 (A) bubbling oxygen through a solution of  $\text{H}_2\text{S}$  in water  

$$2\text{H}_2\text{S} + \text{O}_2 \rightarrow 2\text{H}_2\text{O} + 2\text{S}$$
  
 (B) passing  $\text{H}_2\text{S}$  in very dilute  $\text{HNO}_3$  solution  
 (C) solution of sulphur in alcohol is added to water  
 (D) sulphur is shaken with distilled water
- Ans.** (D)

**Sol.** When sulphur is shaken with water, no colloidal solution is obtained. All other reactions would produce a colloidal solution.

**Q.7**  $\text{Fe}(\text{OH})_3$  is a positively charged colloidal solution. Which of the following would be the most effective for its coagulation?

- (A)  $\text{Na}_3\text{PO}_4$                       (B)  $\text{Na}_2\text{SO}_4$                       (C)  $\text{NaCl}$                       (D)  $\text{AlCl}_3$

**Ans.** (A)

**Sol.** According to Schulze-Hardy rule,  $\text{Na}_3\text{PO}_4$  would be the most effective.

**Q.8** The process of passing a precipitate into colloidal solution on adding an electrolyte is called

- (A) peptisation                      (B) electro-osmosis                      (C) electrophoresis                      (D) dialysis

**Ans.** (A)

**Sol.** The process of throwing a fresh precipitate in a colloidal solution by shaking it with a suitable electrolyte is called peptisation.

**Q.9** Which of the following is a protective colloid?

- (A) gelatin                      (B) blood                      (C) soil                      (D) sulphur

**Ans.** (A)

**Sol.** Only a lyophilic colloid is a protective colloid. When added to a lyophobic colloid, it checks the coagulation of a lyophobic colloid. Gelatin is a lyophilic and so a protective colloid.

**Q.10** Gold number denotes the

- (A) flocculating value of an electrolyte  
(B) peptising power of an electrolyte  
(C) protective power of a lyophilic solution  
(D) electrophoretic movement of colloidal particles

**Ans.** (C)

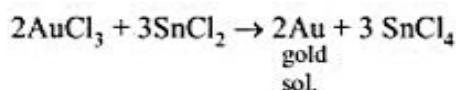
**Sol.** Gold number denotes the protective power of a lyophilic colloid.

**Q.11** What is positive and negative adsorption? What type of substances exhibit positive adsorption?

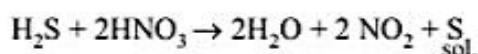
**Sol.** If a substance is dissolved in water and it concentrates more at the surface and less in the bulk, the process is known as positive adsorption. A higher concentration of the substance in the bulk and less at the surface is negative adsorption. Substances like fatty acids, soaps, dyes, etc., show positive adsorption whereas acids, bases, and salts exhibit negative adsorption.

**Q.12** Give one example each where oxidation, reduction, and hydrolysis can be used for the preparation of a colloidal solution.

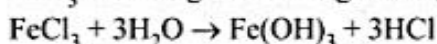
**Sol.** (a) A colloidal solution of gold can be produced by the reduction of  $\text{AuCl}_3$ .



(b) Colloidal sulphur is obtained when  $\text{H}_2\text{S}$  is passed in dilute  $\text{HNO}_3$ . (oxidation process)



(c)  $\text{FeCl}_3$  on boiling with water gives  $\text{Fe}(\text{OH})_3$  solution. (Hydrolysis)





**Q.13** What is coagulation value? How can you compare the coagulating powers of two electrolytes?

**Sol.** The minimum amount of an electrolyte (millimoles) that must be added to one litre of a colloidal solution so as to bring about complete coagulation or flocculation is called coagulation or flocculation value of an electrolyte. Thus the smaller the flocculation value, the greater the coagulating power. As such

$$\frac{\text{Coagulating power of electrolyte I}}{\text{Coagulating power of electrolyte II}} = \frac{\text{Coagulation value of electrolyte II}}{\text{Coagulation value of electrolyte I}}$$

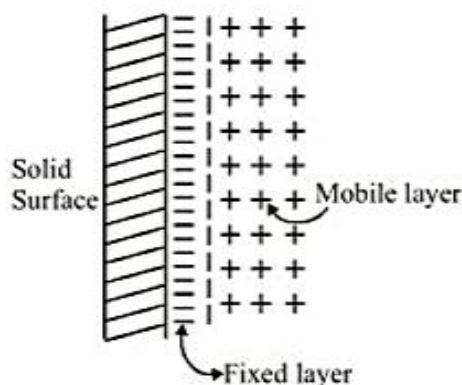
**Q.14** The coagulation of 100 mL of a gold solution is completely prevented by addition of 0.25 g of starch to it before adding 1 mL of 10% NaCl solution. What is the gold number of starch?

**Sol.** Starch added to 100 mL of a gold solution to completely prevent its coagulation by 1 mL of 10% NaCl = 0.25 g or 250 mg.

Therefore, 25 mg of starch would be necessary to prevent coagulation of 10 mL of gold solution and, so, the gold number is 25.0.

**Q.15** What is electrokinetic potential?

**Sol.** A colloidal particle is charged. It carries either a positive or negative charge. During the formation of a colloidal solution, the particle preferentially adsorbs one type of ion on its surface. This forms a fixed layer of charges. To counterbalance it, oppositely charged ions are attracted to form an electrical double layer. This layer is considered to be mobile as shown below.

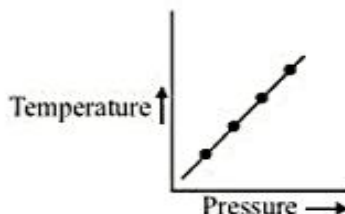


Such a double layer of charges is called Helmholtz double layer. Now it is observed that some of the compensating charges are held in the stationary liquid layer adhering to the surface. The remaining charges are distributed next to this layer in the liquid in the form of a diffuse layer. The potential difference that exists between the stationary layer of compensating charges and the diffuse layer (present in the body of solution) is called electrokinetic or zeta potential.

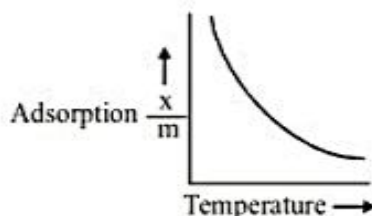
**Q.16** What is an adsorption isostere and adsorption isobar?

**Sol.** Adsorption increases with an increase in pressure and normally decreases with an increase in temperature. Thus, if temperature is increased to a certain value (so that the adsorption decreases) the pressure will have to be increased in order to have the same amount of adsorption.

Obviously, for the same amount of adsorption, the plot between pressure vs temperature should be linear. As such, the plot between temperature vs pressure for a given amount of adsorption is called 'adsorption isostere'.



As stated above, the magnitude of adsorption should increase with a fall in temperature. This actually happens except in chemisorption, where extent of adsorption first increases and then decreases with an increase in temperature. The curve (given below) showing the effect of temperature on the extent of adsorption at a given pressure is called 'adsorption isobar'.



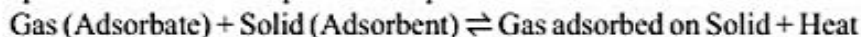
**Q.17** Adsorption of a gas on the surface of solid is generally accompanied by decrease in entropy. Still it is a spontaneous process. Explain.

**Sol.** Adsorption is an exothermic process, i.e., energy factor favours the process. As  $\Delta G = \Delta H - T\Delta S$ , in adsorption, though  $\Delta S$  is -Ve but  $\Delta H$  is also -Ve and  $\Delta H > T\Delta S$  in magnitude so that  $\Delta G$  is -Ve. Hence, the process is spontaneous.

**Q.18** Explain the following giving reasons :

- (i) Rate of physical adsorption decreases with rise of temperature.
- (ii) Cause of Brownian moment.
- (iii) Colloidal particles scatter light

**Sol.** (i) Physical adsorption is an exothermic process in equilibrium



As the temperature is increased, by Le Chatelier's principle, equilibrium shifts in the backward direction, i.e., adsorption decreases.

**Q.19** A one-litre vessel contained a gas at 27°C. 6 g of charcoal was introduced into it. The pressure of the gas fell down from 700 mm to 400 mm. Calculate the volume of the gas (at STP) adsorbed per gram of charcoal. Density of charcoal sample used was 1.5 g cm<sup>-3</sup>.

**Sol.** Volume of the vessel = 1000 cm<sup>3</sup>

$$\text{Volume of charcoal present in the vessel} = \frac{6 \text{ g}}{1.5 \text{ g cm}^{-3}} = 4 \text{ cm}^3$$



$\therefore$  Volume of the gas initially at  $27^\circ\text{C}$ , 700 mm pressure =  $1000 - 4 = 996 \text{ cm}^3$

Volume of the gas at 400 mm and  $27^\circ\text{C}$  is again equal to the volume of the vessel excluding that of charcoal, i.e.,  $996 \text{ cm}^3$ . Let us calculate equivalent volume of the gas at 700 mm at the same temperature

$$P_1 V_1 = P_2 V_2 \text{ i.e. } 400 \times 996 = 700 \times V_2 \text{ or } V_2 = 569.1 \text{ cc}$$

$\therefore$  Volume of the gas adsorbed at  $27^\circ\text{C}$ , 700 mm pressure =  $996 - 569.1 = 426.9 \text{ cm}^3$

$$\therefore \text{ Volume adsorbed per gram of charcoal} = \frac{426.9}{6} \text{ cm}^3 \text{ g}^{-1} = 71.1 \text{ cm}^3 \text{ g}^{-1}$$

Converting this volume to STP we get

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \text{, i.e., } \frac{700 \times 71.1}{300} = \frac{760 \times V_2}{273} \text{ or } V_2 = 59.6 \text{ cm}^3$$

**Q.20** 1 g of charcoal adsorbed 100 ml of 0.5 M  $\text{CH}_3\text{COOH}$  to form a monolayer, and thereby the molarity of  $\text{CH}_3\text{COOH}$  reduces to 0.49 M. Calculate the surface area of the charcoal adsorbed by each molecule of acetic acid. Surface area of charcoal =  $3.01 \times 10^2 \text{ m}^2 \text{ g}^{-1}$ .

**Sol.** 100 ml of 0.5 M  $\text{CH}_3\text{COOH}$  contains  $\text{CH}_3\text{COOH} = 0.05 \text{ mole}$

After adsorption,  $\text{CH}_3\text{COOH}$  present = 0.049 mole

$\therefore$  Acetic acid adsorbed by 1 g charcoal =  $(0.05 - 0.049) \text{ mole} = 0.001 = 6.02 \times 10^{20} \text{ molecules}$

$$\therefore \text{ Surface area of charcoal adsorbed by each molecule} = \frac{3.01 \times 10^2 \text{ m}^2}{6.02 \times 10^{20}} = 5 \times 10^{-19} \text{ m}^2$$

**Q.21** 20% of surface sites are occupied by  $\text{N}_2$  molecules. The density of surface sites is  $6.023 \times 10^{14} \text{ cm}^{-2}$  and total surface area is  $1000 \text{ cm}^2$ . The catalyst is heated to 300 while  $\text{N}_2$  is completely desorbed into a pressure of 0.001 atm and volume  $2.46 \text{ cm}^3$ . Find the active sites occupied by each  $\text{N}_2$  molecule.

**Sol. Step-I :** Calculate of total no. of surface sites

$$\text{Density of surface sites} = 6.023 \times 10^{14} \text{ cm}^{-2}$$

$$\text{Total surface area} = 1000 \text{ cm}^2 = 10^3 \text{ cm}^2$$

$$\therefore \text{ Total no. of surface sites} = (6.023 \times 10^{14}) \times (10^3) = 6.023 \times 10^{17}$$

**Step-II :** Calculation of surface sites occupied by  $\text{N}_2$  molecules.

$$\text{Surface sites occupied by } \text{N}_2 \text{ molecules} = \frac{20}{100} \times 6.023 \times 10^{17} = 1.2046 \times 10^{17}$$

**Step-III :** Calculation of total no. of  $\text{N}_2$  molecules

$$P = 0.001 \text{ atm, } V = 2.46 \text{ cm}^3 = 2.46 \times 10^{-3} \text{ L, } T = 300 \text{ K}$$

$$PV = nRT \text{ or } n = \frac{10^{-3} \text{ atm} \times 2.46 \times 10^{-3} \text{ L}}{0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 300 \text{ K}} = 10^{-7} \text{ mole}$$

$$\therefore \text{ No. of molecules} = (10^{-7}) \times (6.023 \times 10^{23}) = 6.023 \times 10^{16}$$

**Step-IV :** Calculation of no. of sites occupied by each  $\text{N}_2$  molecule

$$= \frac{\text{No. of sites occupied}}{\text{No. of } \text{N}_2 \text{ molecules}} = \frac{1.2046 \times 10^{17}}{6.023 \times 10^{16}} = 2$$



## AROMATIC HYDROCARBONS

### MAIN SOURCE

Bituminous coal when subjected to destructive distillation in the absence of air [1000°–1200°C] the chief constituent obtained is coal tar.

**Fractional distillation of coal tar :** Different fractions are :

	Fraction	Temperature	Main constituents
(a)	Light oil	80 – 170°C	Benzene, toluene, xylene etc.
(b)	Middle oil (carbolic oil)	170° – 230°C	Naphthalene, Phenol etc.
(c)	Heavy oil	230° 270°C	Cresols, naphthalene
(d)	Green oil	270° – 360°C	Anthracene
(e)	Pitch	Residue	Carbon

### BENZENE

[i] Discoverer : Michael Faraday

[iii] Geometry – Hexagonal

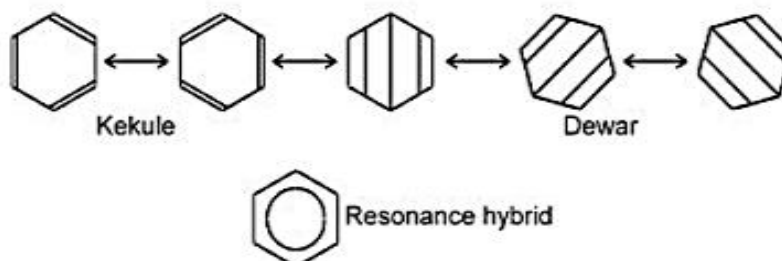
[v] C–C Bond length : 1.39 Å

[vii] Resonance in benzene :

[ii] C–hybridisation :  $sp^2$

[iv] Bond angle : 120°

[vi] C–H Bond length : 1.09 Å

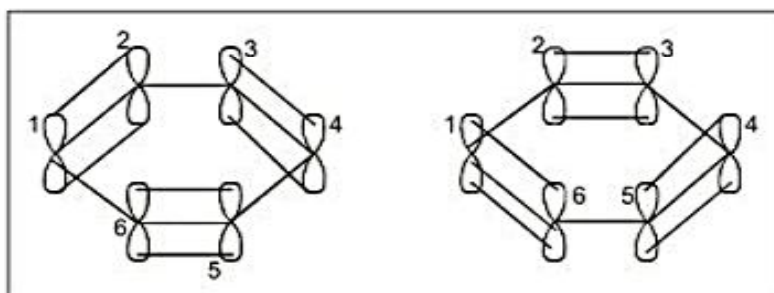


[ix] Number of angles of 120° : 18

[x] Localized and delocalized  $\pi$ -orbital

**Localized  $\pi$ -orbital**

**Localized  $\pi$ -orbital**

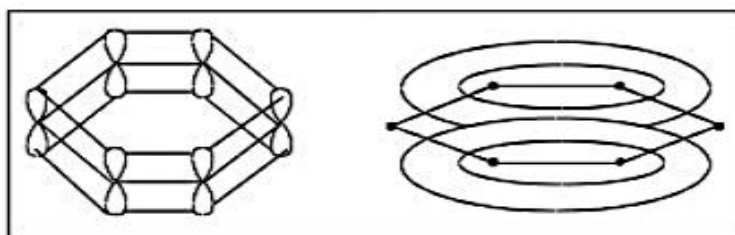


Partial overlapping  
of p-orbital  $C_1-C_2$ ,  
 $C_3-C_4$  and  $C_5-C_6$

Partial overlapping  
of p-orbital  $C_2-C_3$ ,  
 $C_4-C_5$  and  $C_1-C_6$

Obviously, each orbital formed in the partial overlapping is attracted by two carbon nucleus hence less stable.

### Delocalized p-orbital :



### Methods of Preparation of Benzene :

#### Isolation From 'Light Oil Fraction – Industrial method :

In 'light oil', at least 60–65% benzene is present. Alkaline impurities (aniline, pyridine, quinoline, etc.) are removed by washing 'light oil' with cold and conc.  $H_2SO_4$ . The acidic impurities are removed by washing with dilute NaOH solution. After that, NaOH is removed by washing with water. Three fractions are obtained at different temperature ranges by fractional distillation of the neutral sample of oil.

[i] 90% Benzol (90's benzol). 80–110°

[ii] 50% Benzol (50's benzol). 110–140°

[iii] Solvent naphtha – 140°–170°

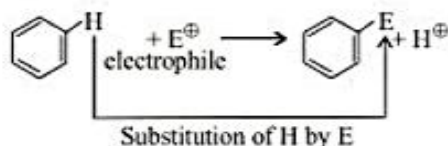
The 90% benzol contains about 70% benzene 24% toluene and remaining xylenes. Fractional distillation gives benzene at 80°, toluene at 110° and a mixture of all the three xylenes at 137–145°. Crystals are formed on cooling benzene from which pure benzene can be obtained by melting the crystals.

### ELECTROPHILIC AROMATIC SUBSTITUTION (EAS)

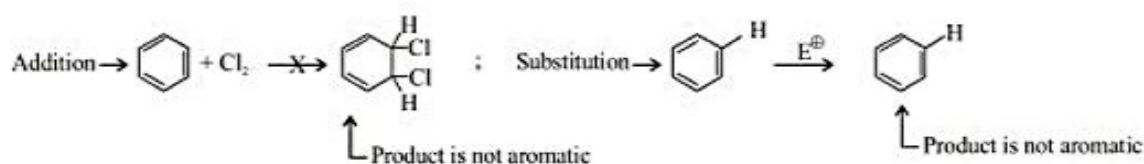
Based on its structure and properties, what kind of reaction should benzene undergo ? Are any of its bond particularly weak does it have electron rich or electron deficient atom.

- \* Benzene has six p-electron delocalized in six p-orbitals that overlap above and below the plane of ring. These loosely held  $\pi$ -electron make the benzene ring electron rich, and so it reacts with electrophile.
- \* Because benzene six  $\pi$ -electron satisfy Huckel's rule, benzene is especially stable. Reactions that keep the aromatic ring intact are therefore, favoured.
- \* Electron cloud above and below the plane of benzene shields the ring carbon from the attack of a nucleophile.

As a result, the characteristic reaction of benzene is electrophilic aromatic substitution - a hydrogen atom is replaced by an electrophile.



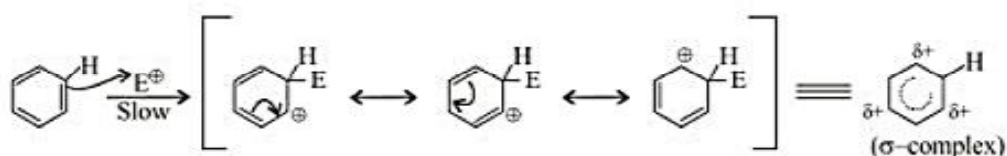
Benzene does not undergo addition reaction like other unsaturated hydrocarbons, because addition would yield a product that is not aromatic. Substitution of a hydrogen on the other hand, keeps the aromatic ring intact.



## THE GENERAL MECHANISM OF EAS

EAS reactions occur via a two steps mechanism.

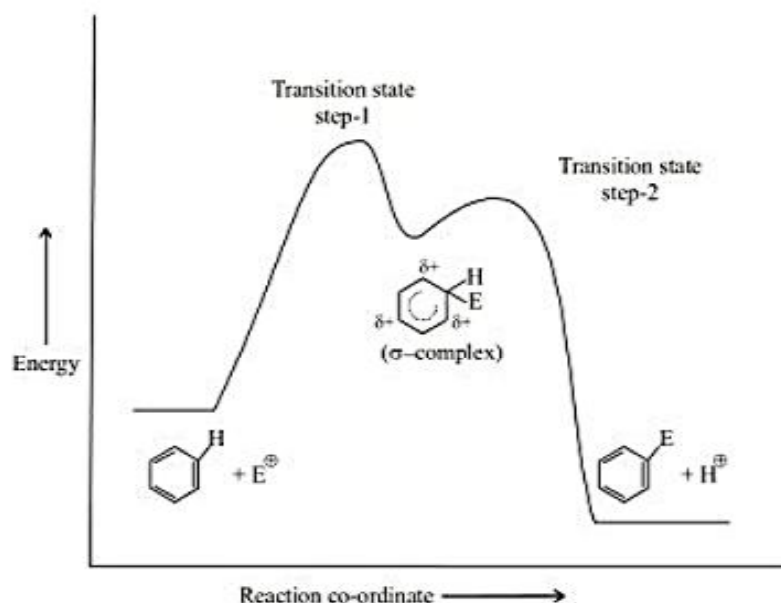
### Step 1. Addition of the electrophile



### Step 2. Loss of a proton to reform the aromatic ring



Any of the three resonance structures of the carbocation intermediate can be used to draw the product. The energy changes in EAS are shown in figure. The mechanisms consist of two steps, so energy diagram has two energy barriers. Because the first step is rate-determine, its transition state is higher in energy.





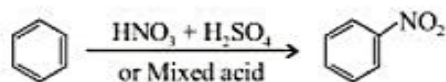
Most examples of EAS proceed by this sequence of events :

1. Generation of an electrophile
2. Attack of the aromatic ring on the electrophile
3. The resulting carbocation is stabilized by the resonance
4. A proton is eliminated from the carbocation
5. A substituted aromatic compound is formed

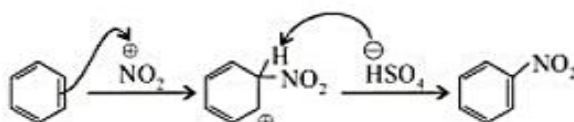
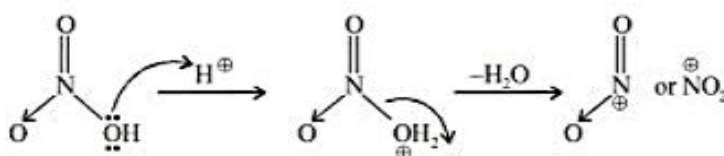
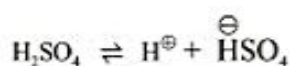
## NITRATION OF BENZENE

The introduction of a nitro ( $-\text{NO}_2$ ) group on benzene known as nitration of benzene. The most common reagent for the nitration of aromatic compound is mixture of concentration  $\text{HNO}_3$  and concentration  $\text{H}_2\text{SO}_4$  (mixed acid).

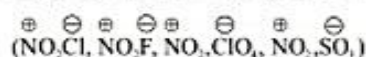
The electrophile required for the nitration is nitronium ion ( $^+\text{NO}_2$ ).



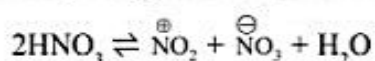
**Mechanism :**



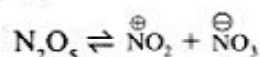
Besides mixed acid, other reagents have also been used for nitration such as nitronium salts



In the case of fuming  $\text{HNO}_3$  alone  $^+\text{NO}_2$  is formed as follow



In nonpolar solvent  $\text{N}_2\text{O}_5$  get dissociated and produces  $^+\text{NO}_2$



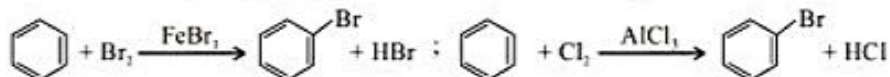
**Problem :** Compare rate of nitration among  $\text{C}_6\text{H}_6$ ,  $\text{C}_6\text{D}_6$  and  $\text{C}_6\text{T}_6$ .

**Solution :**  $\text{C}_6\text{H}_6 = \text{C}_6\text{D}_6 = \text{C}_6\text{T}_6$

Therefore nitration of benzene does not shows primary kinetic isotopic effect.

## HALOGEN OF BENZENE

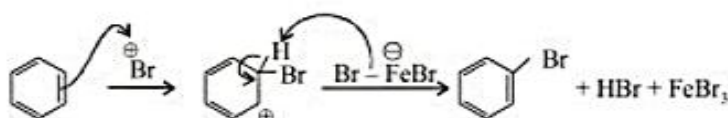
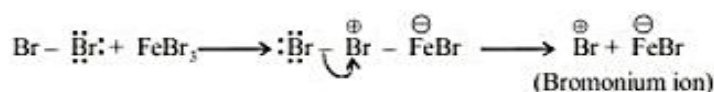
The introduction of halo ( $-X$ ) group on benzene known as halogenation of benzene



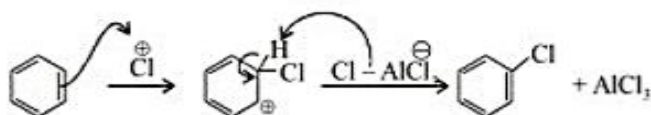
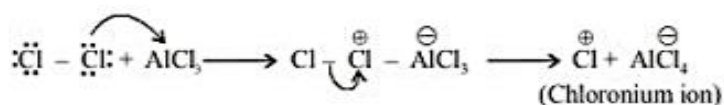
The bromination or chlorination of benzene requires a Lewis acid catalyst such as  $\text{FeBr}_3$ ,  $\text{AlBr}_3$ ,  $\text{FeCl}_3$  or  $\text{AlCl}_3$ .

Sometime Fe or Al is used but real catalyst is not Fe or Al itself but  $\text{FeX}_3$  or  $\text{AlX}_3$  is formed from the reaction between halogen and Fe or Al.

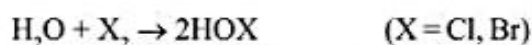
### Mechanisms for Bromination



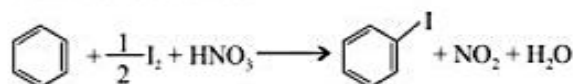
### Mechanisms for Chlorination



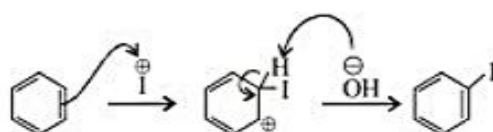
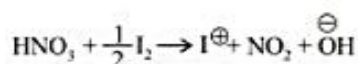
Bromination and chlorination also occur by  $\overset{\ominus}{\text{HOBr}}$  and  $\overset{\oplus}{\text{HOCl}}$ , obtained by reaction between  $\text{H}_2\text{O}$  and  $\text{X}_2$ .



Iodination of benzene requires an acidic oxidizing agent such as nitric acid. Nitric acid is consumed in the reaction, so it is a reagent rather a catalyst.



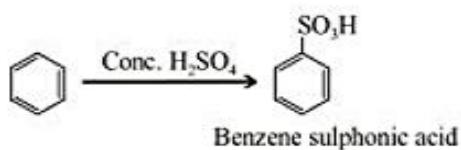
### Mechanisms for Iodination



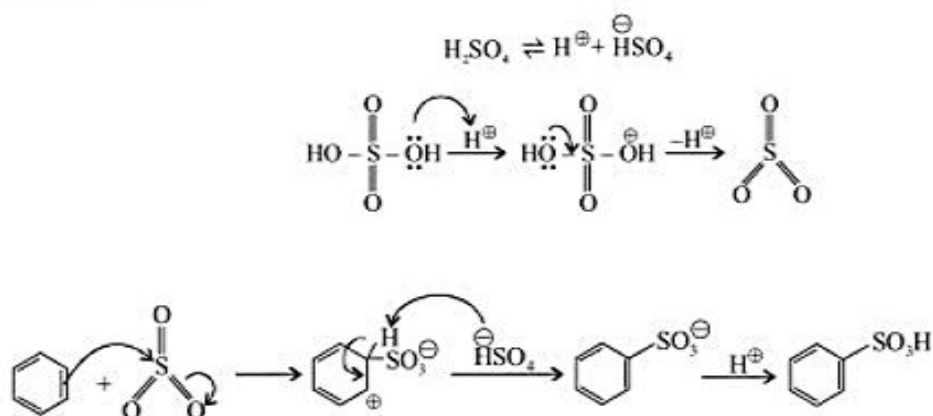
The electrophile required for halogenation reaction is halonium ion ( $\text{X}^{\oplus}$ )

### Sulphonation of Benzene

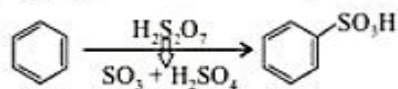
Sulphonation is usually done with concentration  $\text{H}_2\text{SO}_4$ . Electrophile required for sulphonation reaction is  $\text{SO}_3$ .



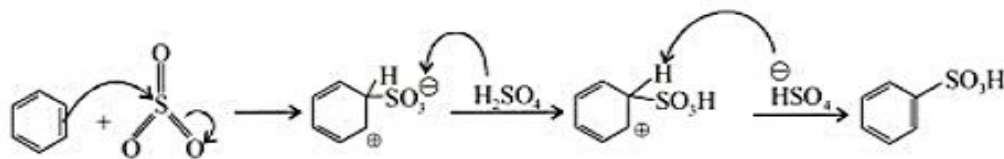
#### Mechanisms :



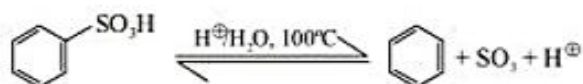
Fuming sulphuric acid or oleum ( $\text{H}_2\text{S}_2\text{O}_7$ ) is also used to sulphonate aromatic ring.



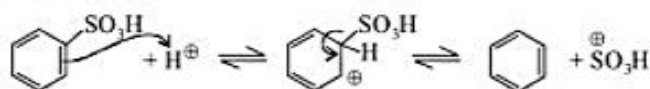
#### Mechanisms :



Sulphonation of benzene is a reversible reaction. If benzenesulfonic acid is heated in dilute acid, the reaction proceeds in reverse direction.



#### Mechanisms of desulphonation

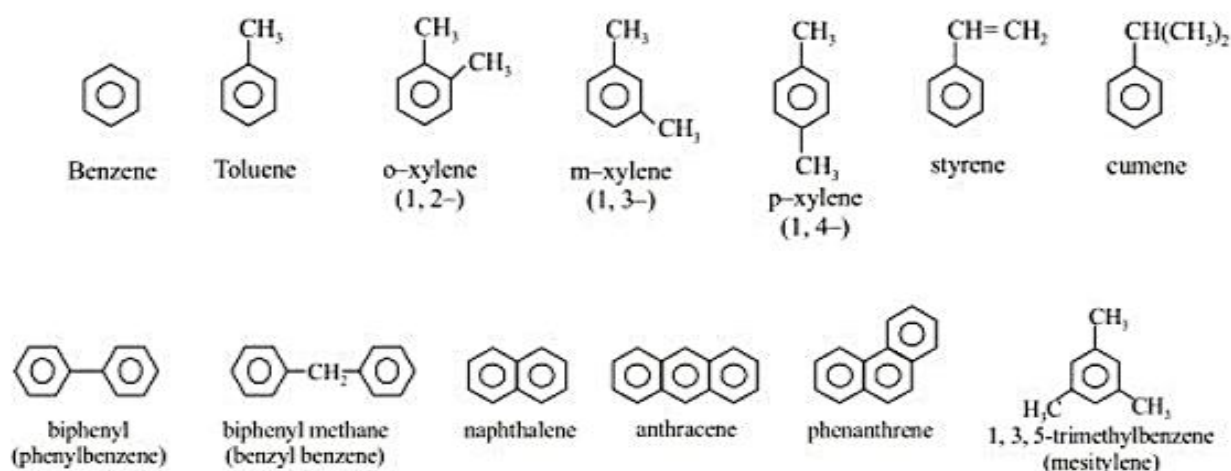




## RELATIVE REACTIVITY OF SUBSTITUTED BENZENE

Ortho para directors Strongly activating	Meta directors Moderately deactivating
$-\text{O}^{\ominus}, -\ddot{\text{N}}\text{H}_2, -\ddot{\text{N}}\text{R}_2, -\ddot{\text{O}}\text{H}, -\ddot{\text{O}}\text{R}$ Moderately activating $-\ddot{\text{N}}\text{H}-\overset{\text{O}}{\parallel}-\text{CH}_3, -\ddot{\text{O}}-\overset{\text{O}}{\parallel}-\text{CH}_3$ Weakly activating $-\text{CH}_3, -\text{CH}_2\text{CH}_3, -\text{R}$ $-\text{C}_6\text{H}_5, -\text{CH}=\text{CH}_2$ Weakly deactivating $-\ddot{\text{F}}:, -\ddot{\text{Cl}}:, -\ddot{\text{Br}}:, -\ddot{\text{I}}:$	$-\overset{\text{O}}{\parallel}-\text{H}, -\overset{\text{O}}{\parallel}-, -\overset{\text{O}}{\parallel}-\text{Cl}, -\overset{\text{O}}{\parallel}-\text{NH}_2, -\overset{\text{O}}{\parallel}-\text{OH}, -\overset{\text{O}}{\parallel}-\text{OR}$ Strongly deactivating $-\text{NH}_3^{\oplus}, -\text{NR}_3^{\oplus}, -\text{NO}_2, -\text{C}\equiv\text{N}, -\text{CF}_3, -\text{CCl}_3$

## AROMATIC HYDROCARBONS



### Source

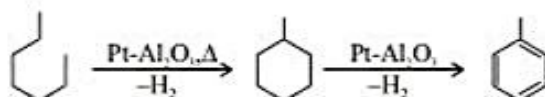
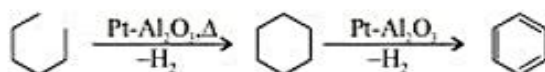
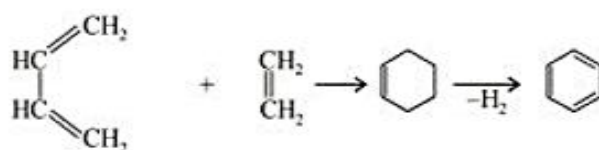
#### (a) Fractional distillation of Coaltar

The dark-brown sticky liquid called coal-tar is a mixture of several aromatic hydrocarbons, phenols, bases etc. The first step in the separation of coal-tar into its components is distillation in a fractionating column as given in table.

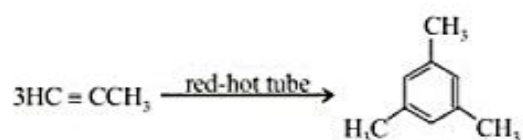
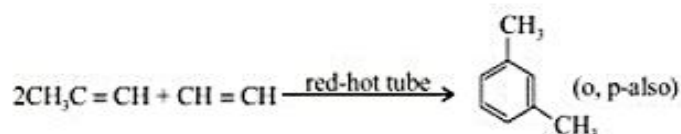
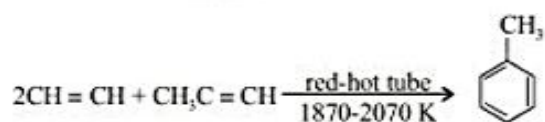
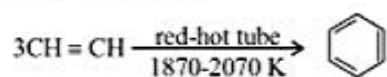
#### (b) High temperature cracking

Petroleum (kerosene and low boiling fractions)  $\xrightarrow{\text{cracking}}$  mixture of alkenes and alkanes.

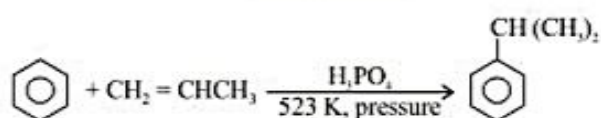
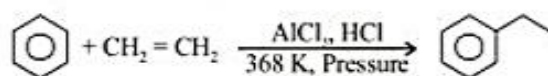
$\xrightarrow{\text{cyclisation/aromatization}}$  aromatic hydrocarbon



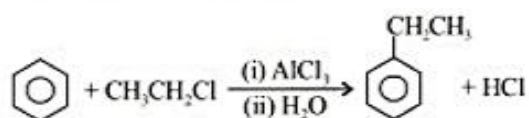
**(c) Polymerisation**



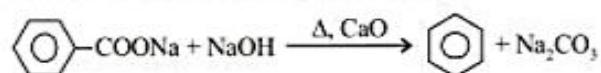
**(d) Alkyl benzene synthesis**

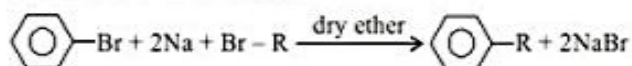
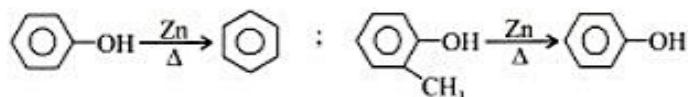
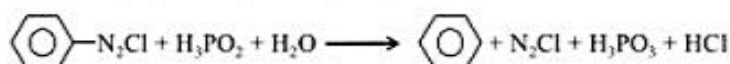
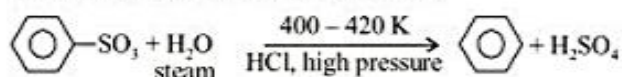


**(e) Friedel-Crafts reaction**



**(f) Decarboxylation of Aromatic acids**



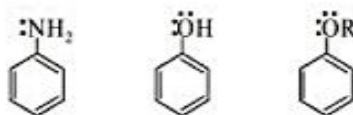
**(g) Wurtz-Fitting reaction****(h) Deoxygenation of Phenols****(i) Reduction of Diazonium salts****(j) Desulphonation of sulphonic acids**

Mechanisms of the above reactions have been given in further section.

1. All meta-directing groups are deactivating groups;
2. All ortho, para-directing groups except for the halogen are activating groups.
3. The halogens are deactivating groups

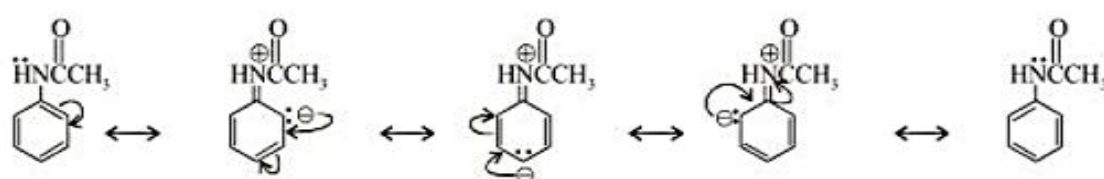
The activating substituents make the benzene ring more reactive towards electrophilic substitution, the deactivating substituents make the benzene ring less reactive towards electrophilic substitution.

All the strong activating substituents donate electrons into the ring by resonance and withdraw electrons inductively. The fact that they are strong activators indicate that electron donation into the ring by resonance (which increases electron-density hence, nucleophilicity) is much greater than electron withdrawal from the ring by the inductive effect (which decreases electron-density hence nucleophilicity). Strongly activating substituents are :

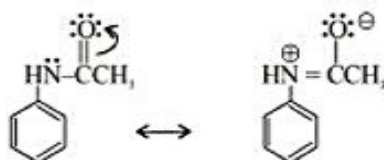


The moderately activating substituents also donate electrons into the ring by resonance and withdraw electrons from the ring inductively. However they donate electrons into the ring by resonance less effectively than do not strongly activating substituents. These substituents are less effective at resonance donation since, they can donate electrons by resonance in two competing directions- into the ring and away from the ring and thus net resonance effect is diminished and still electron donation by resonance is more than the electron withdrawal by induction and thus, these substituents are activators though moderately.



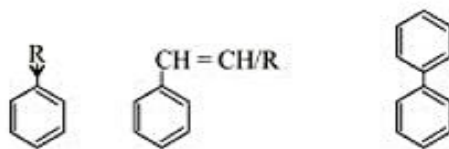


(substituents donate electrons by resonance into the benzene ring)



(substituents donate electrons away from the benzene ring)

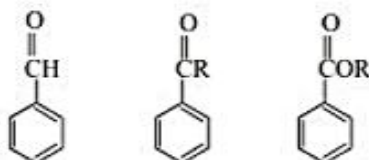
Alkyl, aryl and  $\text{CH}=\text{CHR}$  groups are weakly activating substituents. Two of the three groups (aryl and  $\text{CH}=\text{CHR}$ ) can donate electrons into the ring by resonance and can also withdraw from the ring by resonance. The fact that they are weak activators indicates that they are slightly more electron-donating than they are electron-withdrawing. An alkyl substituent is a weak electron donor because of hyperconjugation.



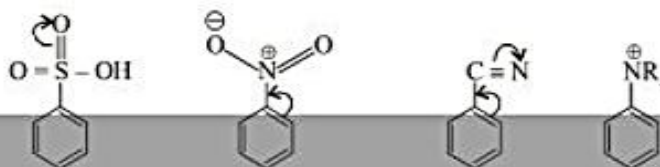
The halogens are weakly deactivating substituents. They donate electrons into the ring by resonance and withdraw electrons inductively. Since, they have been found deactivators, we can conclude that they withdraw electrons inductively more strongly than they donate electrons by resonance.

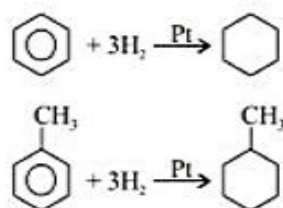


The moderately deactivating substituents all have carbonyl groups directly attached to the benzene ring. They withdraw electron both inductively and by resonance.

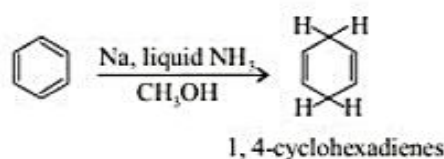


The strongly deactivating substituents are powerful electron withdrawers. With the exception of  $-\text{NH}_2$ ,  $-\text{NH}_2^+$ ,  $-\text{R}$ ,  $-\text{NHR}$ , and  $-\text{NR}$ , and they withdraw electrons both inductively and by resonance. The ammonium ions have no resonance effect, but the positive charge on the nitrogen atom causes them to strongly withdraw electron inductively.

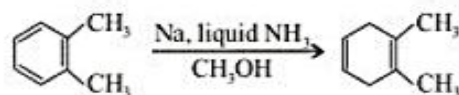
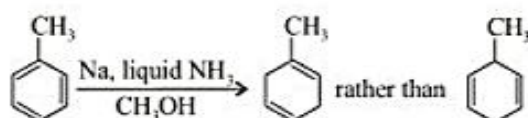


**(a) Catalytic hydrogenation**

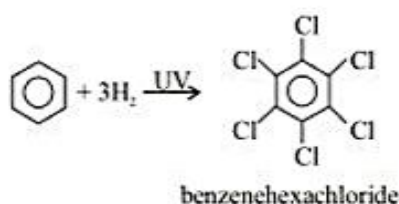
Treatment of arenes with group I metal (like sodium, lithium) and methanol (or ethanol) in liquid reduces arenes to non-conjugated dienes.



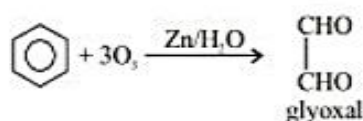
Alkyl substituted arenes give 1, 4-cyclohexadienes in which the alkyl group is a substituent on the double bond.



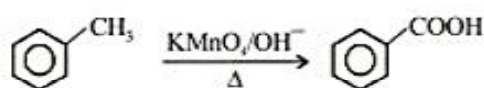
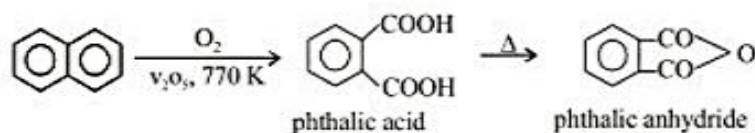
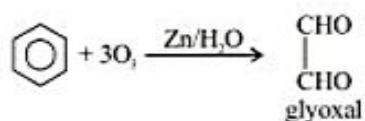
Metal ammonia -alcohol reduction of aromatic ring is known as Birch reduction and is one type of a more general class of reactions called dissolving metal reduction.

**(b) Addition of Halogen**

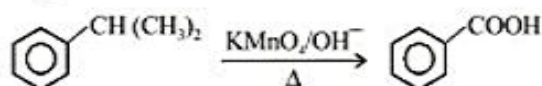
Benzenehexachloride (BHC,  $\text{C}_6\text{H}_6\text{Cl}_6$ ) is also called Lindane or Gammaxene ( $\gamma$ -isomer) and is used insecticide.

**(c) Ozonolysis**

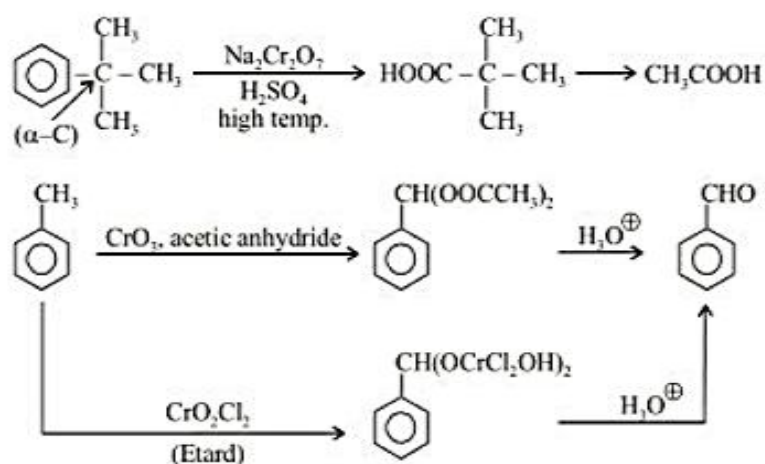
## (d) Oxidation



When oxidised using  $\text{KMnO}_4/\text{OH}^-$ ,  $\text{Na}_2\text{Cr}_2\text{O}_7/\text{H}^+$ ,  $\text{KMnO}_4/\text{H}^+$  the entire side chain, with at least one H at  $\alpha$ -C, regardless of length is oxidised to  $-\text{COOH}$ .



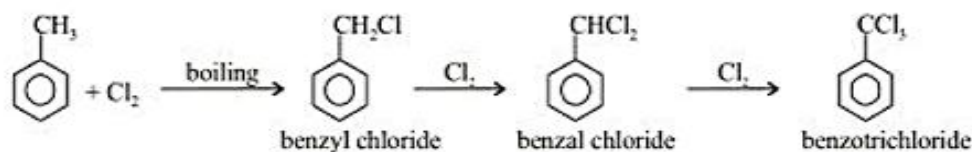
The conversion of alkyl benzenes to benzoic acid with strong oxidations suggest that benzene ring is more stable than the side chains; this is correct so long as the side-chain contains at least one benzylic C-H bond. The first step in the mechanism is the removal of hydrogen from the benzylic carbon. If the side-chain has no C-H bond at the  $\alpha$ -carbon (w.r.t. benzene nucleus), then benzene ring is cleaved.



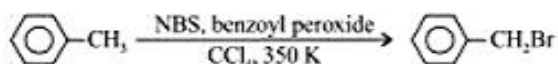
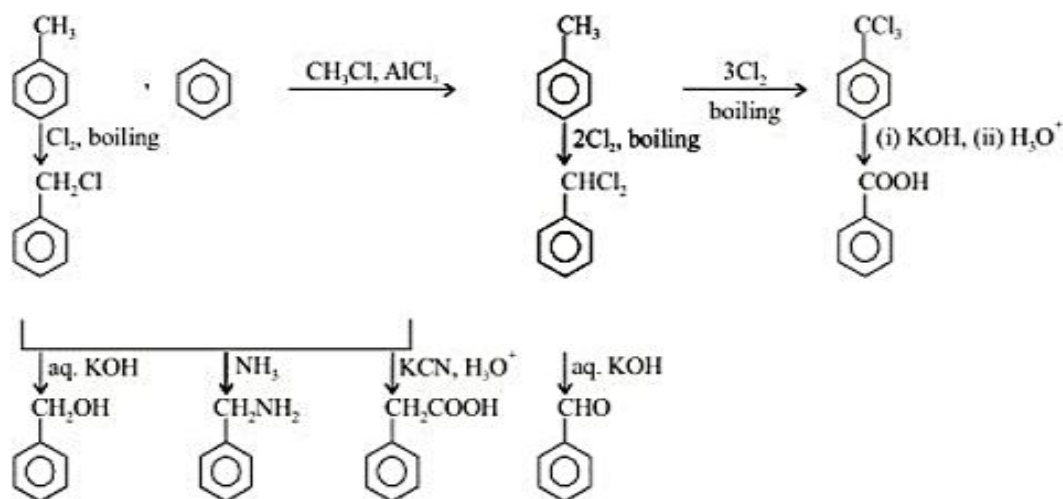
## (e) Combustion





**(f) Side-chain halogenation**

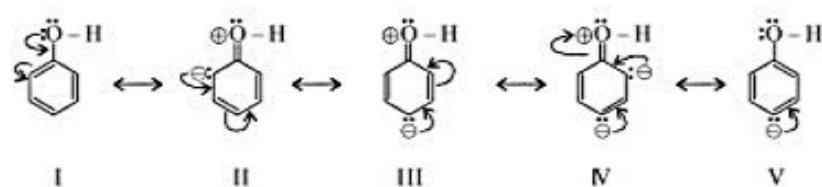
This provides a source of preparing other derivatives from benzene and toluene.



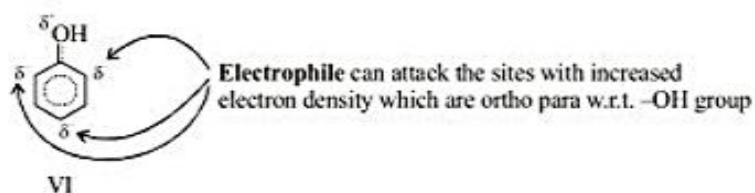
(NBS is N-bromo succinimide)

**DIRECTING INFLUENCE AS DECIDED BY ELECTRON DENSITY**

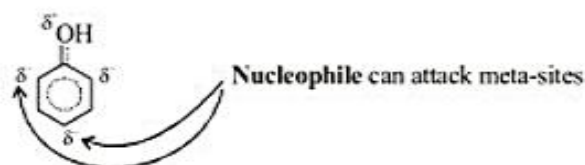
•  $-\text{OH}$  group is ortho and para-directing since it increases electron-density at ortho and para-positions for electrophilic attacks; electron-density at meta-position is decreased hence, electrophilic attack at this position is least.



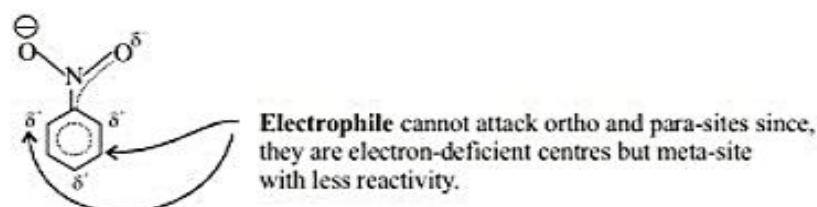
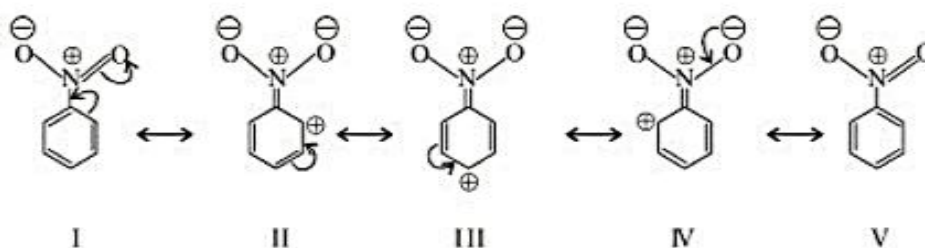
I to V are different resonance structures and VI resonance hybrid structure.



Naturally nucleophile cannot attack ortho and para-sites but can attack at meta-site (but less reactive)



- $-\text{NO}_2$  group is electron-withdrawing group. It deactivates ortho and para-position for electrophilic attack and thus electrophile can occupy meta-position. I to V are resonance and VI is resonance hybrid.

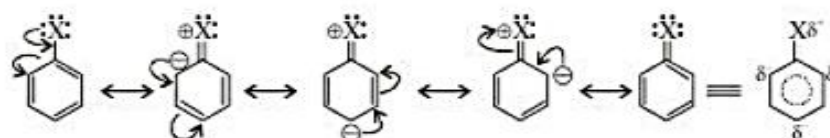


In this case nucleophilic attack at electron-rich ortho and para-sites is favoured.

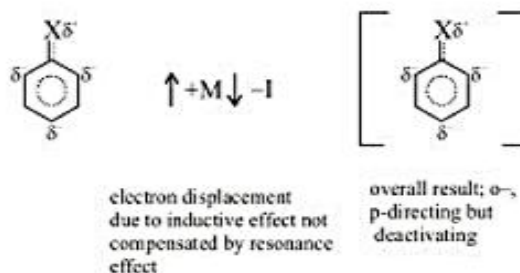


## ANAMALOUS BEHAVIOUR OF HALOGEN SUBSTITUENT

- $\text{X}(\text{F}, \text{Cl}, \text{Br}, \text{I})$  is o-, p-directing but is **deactivating** group.

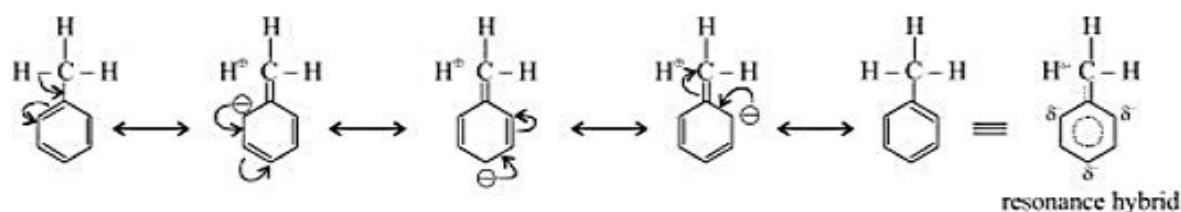


This deactivating nature is attributed to high electronegativity of the halogen atom due to which they withdraw electrons; resonance effect explains its electron-donating behaviour.



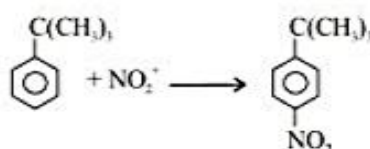
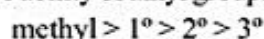
### Alkyl groups and Orientation

Alkyl groups ( $-\text{CH}_3$ ,  $-\text{CH}_2\text{CH}_3$ , etc.) have complete octet and are without one-pair of electrons; but they are ring activators and o-, p-directors. They not only show electron-pumping effect, but also when attached to conjugated system show hyperconjugated effect (no-bond resonance). This type of resonance requires the interaction of  $\sigma$ -electrons instead of usual lone-pair of electrons. In toluene, hyperconjugation is shown below :



Thus, hyperconjugation helps in increasing-density at o-and p-sites in case of alkyl groups.

There must be at least one H-atom on the carbon of the alkyl group joined to the ring carbon to take part in hyperconjugation and relative ability of alkyl groups for this effect is

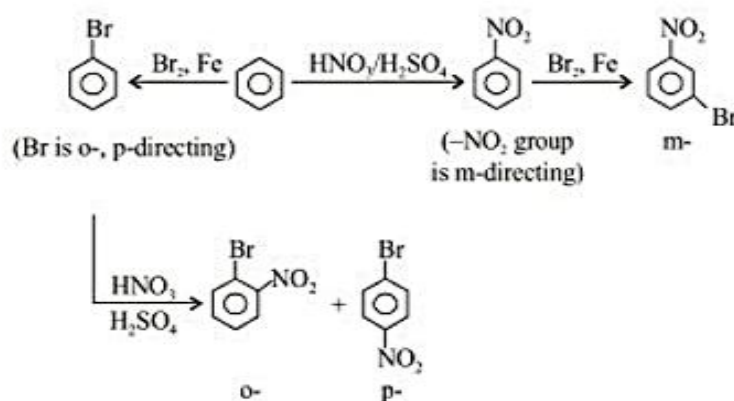


In this case, only p-isomer is obtained. It is due to steric influence of the substituents  $-\text{C}(\text{CH}_3)_3$  and due to its inability to show hyperconjugation.

### Orientation and Synthesis

By using the nature of directing group (substituent), it is possible to prepare variety of products.

To prepare meta-bromo nitrobenzene from benzene, we have to first carry out nitration and then bromination; and to prepare o- and p-derivatives, sequence will be bromination and then nitration.

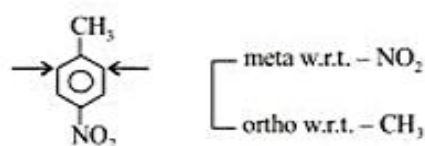


### Orientation in Disubstituted benzene

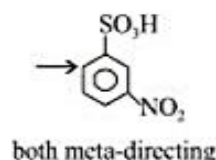
When two substitution are present, orientation of the third coming  $\text{S}_\text{E}$  is complicated.

$-\text{CH}_3$  group is o-, p-directing and  $-\text{NO}_2$  group is m-directing, thus in p-nitrotoluene, new electrophile can be in a position shown by arrow :

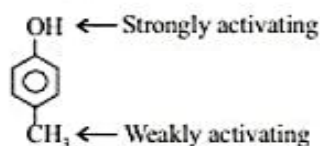




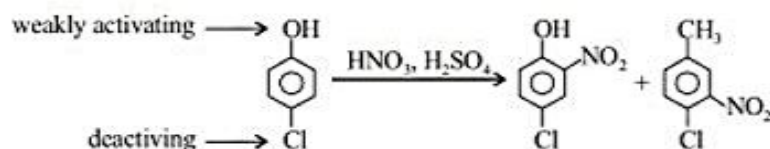
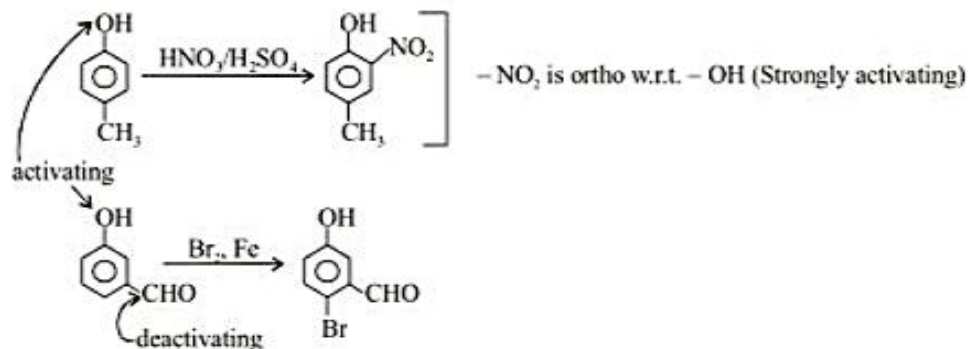
Similarly we can decide the position of the new electrophile in other disubstituted compounds.



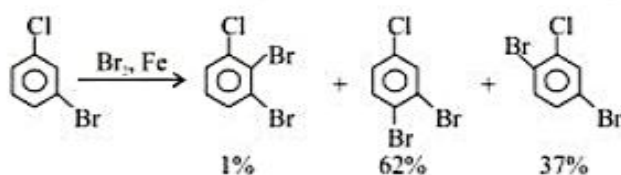
**Problems may arise in the following cases :**



Both are ortho, para-directing and none of the vacant positions are ortho-and para, w.r.t. each. In such cases we follow : (a) Strongly activating groups generally win over deactivating or weakly activating groups.



(b) If the substitution are meta to each other,  $S_E$  in between vacant sites takes place rarely.

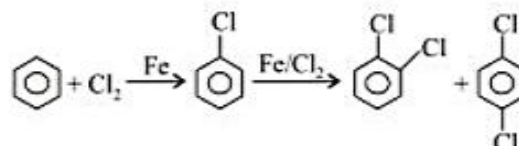


## HALOGEN COMPOUND

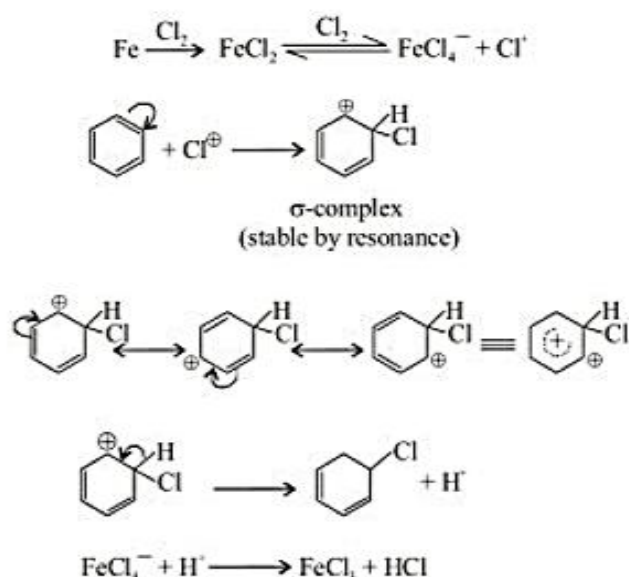
### Aryl Halides

#### Source/Preparation

- Direct halogenation :

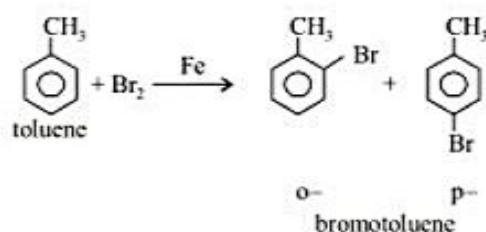


Low temperature and the presence of a halogen carrier favour nuclear substitution. The chlorides or bromides of Al, Fe, Sb may use used :

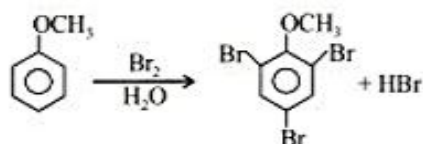


Iron is most commonly used being converted to Lewis acid  $\text{FeCl}_3$  as shown above.

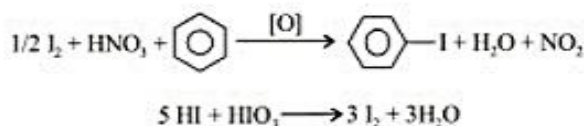
It is again  $\text{S}_\text{E}$  reaction and without halogen-carrier (Lewis acid),  $\text{Cl}^+$  (halonium) is not formed and hence, reaction is not possible :



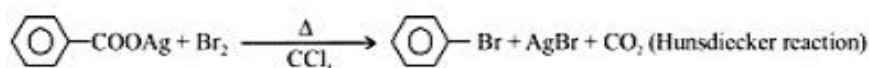
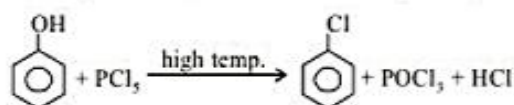
A methoxy group is so strongly activating that anisole quickly bromines in water without a catalyst :



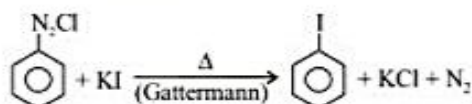
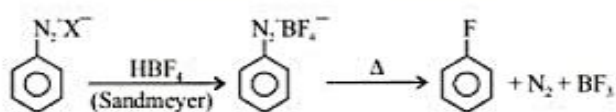
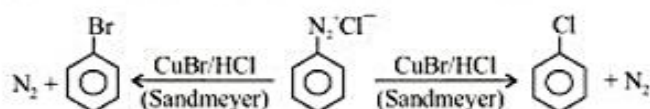
Direction iodination is not possible since, iodine is least reactive and HI formed makes reaction reversible. In presence of oxidising agents like  $\text{HNO}_3$  or  $\text{HIO}_3$ , iodination of benzene is possible and HI formed is converted to  $\text{I}_2$ :



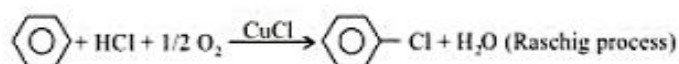
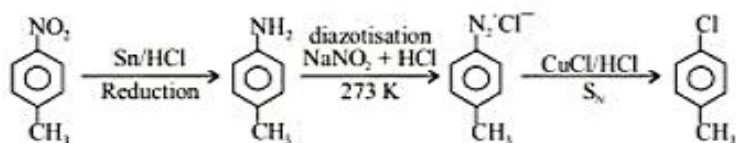
Iodination probably involves an electrophilic aromatic substitution with iodonium ( $\text{I}^+$ ) acting as the electrophile.  $\text{I}^+$  is formed from iodine by oxidation with  $\text{HNO}_3$ ,



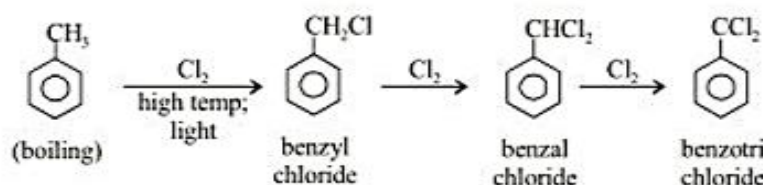
**Diazonium salts are converted to halogen compounds :**



Diazonium salts are obtained by diazotisation of amino compounds and this provides a better route to convert amino compounds into halogen compounds :

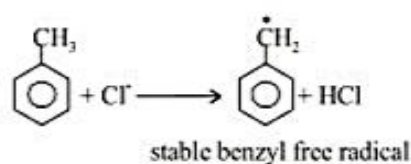


### Side-Chain Derivatives

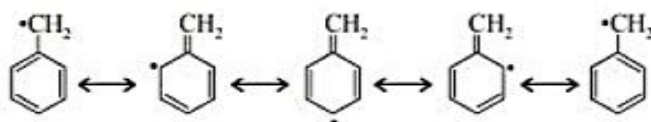


Side-chain halogenation involves free radical mechanisms due to lower bond energy of the benzyl C-H bond :

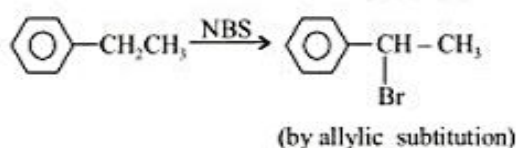




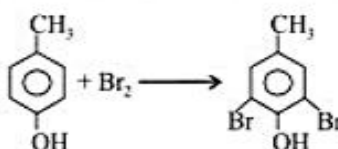
Benzyl radical is stabilised by resonance due to delocalisation of odd electrons into ring :



NBS can also be used for bromination of side-chain alkyl group :



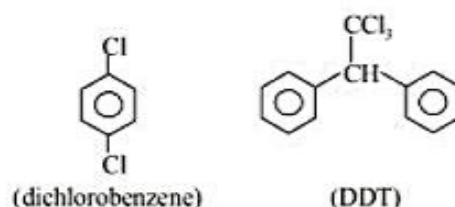
In presence of an activating group –OH or –NH<sub>2</sub>, side chain halogenation is difficult :



## Properties

### Physical

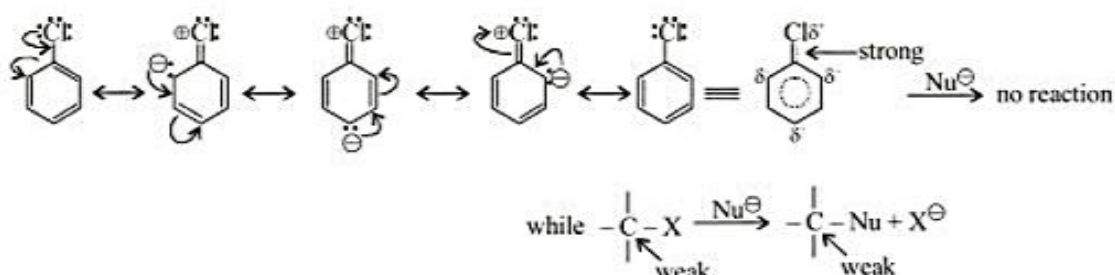
- Less polar, insoluble in water but soluble in organic solvents like ethanol and ether.
- They show physiological activity and are used as insecticides. Examples are :



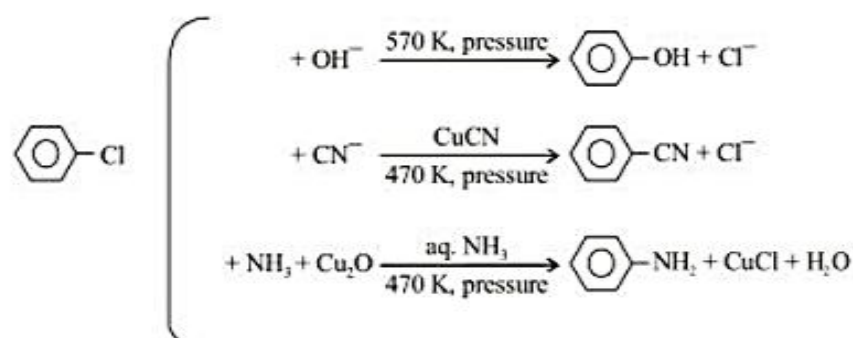
## Chemical

### (a) Low reactivity of Aryl halide for S<sub>N</sub> reaction

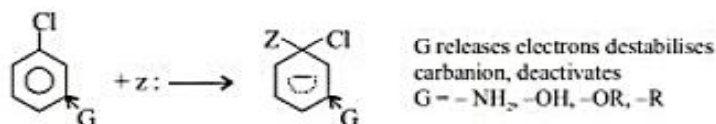
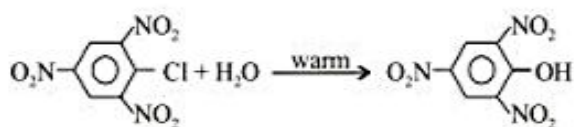
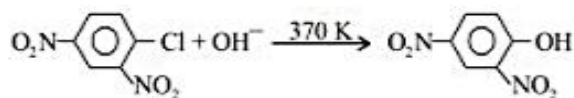
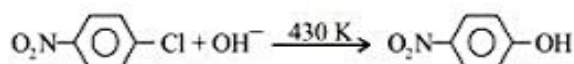
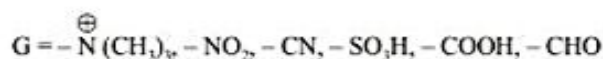
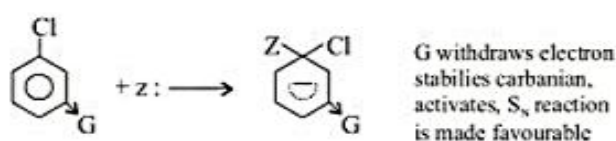
C–X bond in aryl halide is stable due to delocalisation of electrons by resonance. Also (C–X) bond possesses a double bond character like vinyl chloride and is stronger than C–X bond in alkyl halide.



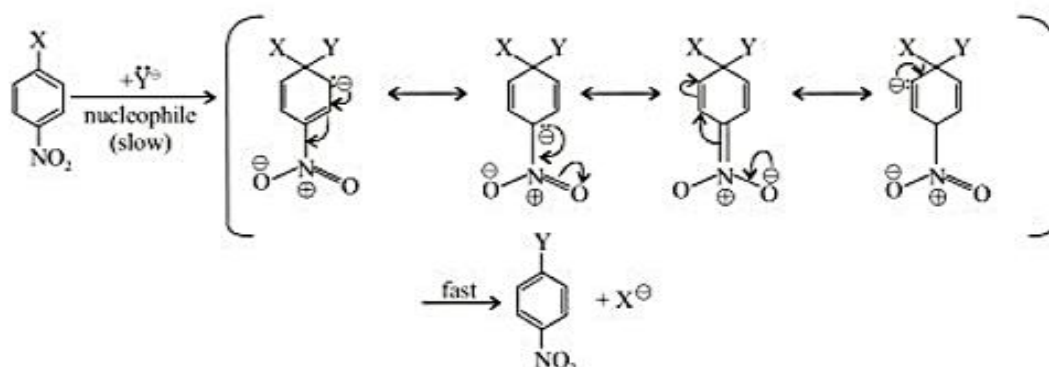
Hence,  $S_N$  reaction is not possible in benzene nucleus under ordinary conditions. However, under high temperature and pressure,  $S_N$  reaction is made possible.



If the benzene ring has (1) one or more substituents that strongly withdraw electrons from the ring by resonance, and (2) a good leaving group (such as halogens), nucleophilic aromatic substitution reactions can occur without using extreme conditions. These electron-withdrawing groups must be positioned ortho or para to the leaving group. The greater the number of electron-withdrawing substituents, the easier it will be to carry out the nucleophilic aromatic substitution reactions.



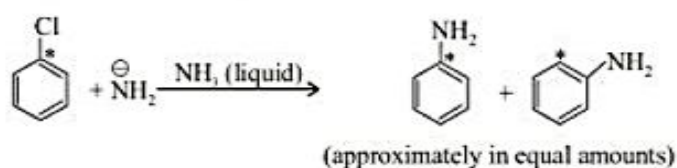
Nucleophilic aromatic substitution takes place by a two-step reaction known as an  $S_N \text{Ar}$  reaction by following mechanisms:



### (b) Elimination-Addition Through Benzyne Intermediate

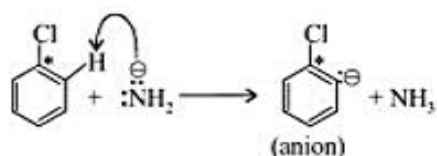
An aryl halide can undergo a nucleophilic substitution reaction in the presence of a very strong base such as  $\text{NH}_2^-$ .

When chlorobenzene – that has the carbon to which chlorine is attached isotopically labelled with  $^{14}\text{C}$  – is treated with amide ion in liquid ammonia, aniline is obtained as a product. Half of the product has the amino group attached to the isotopically labelled carbon (\*) as expected, but the other half has the amino group attached to the carbon adjacent to the labelled carbon.

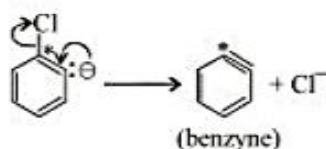


The mechanisms that accounts for the experimental observations involves formation of a benzene intermediate which has two equivalent carbon atoms to which amino group can be attached. Benzyne has an extra  $\pi$ -bond between two adjacent carbon atoms of benzene and can be formed as :

**Step-I :** Strong base  $\text{NH}_2^-$  removes a proton from the position ortho to halogen :

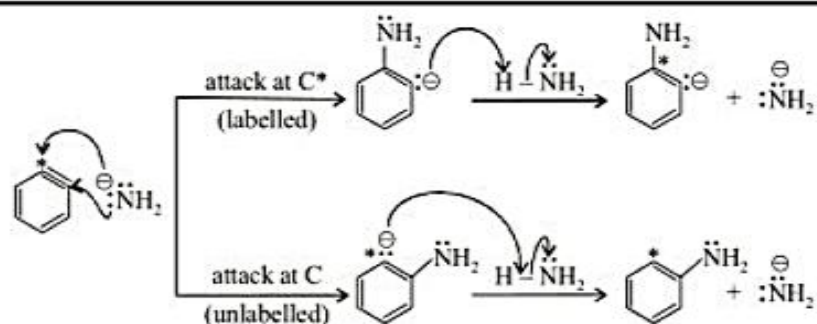


**Step-II :** Anion formed in step I eliminates the halide ion, thereby forming benzyne :

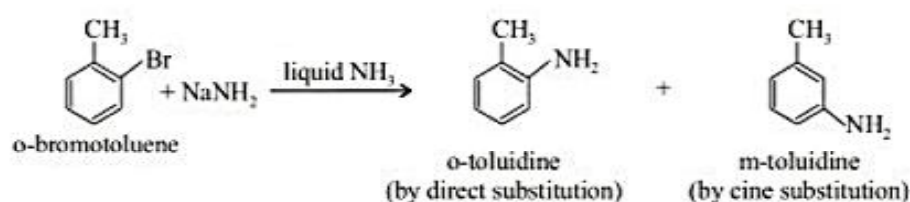


The incoming nucleophile can attack either of the carbons of the “triple bond” of benzyne. Protonation of the resulting anion form the substitution product. The overall reaction is an elimination-addition reaction; benzyne is formed in an elimination reaction and immediately undergoes an addition reaction.

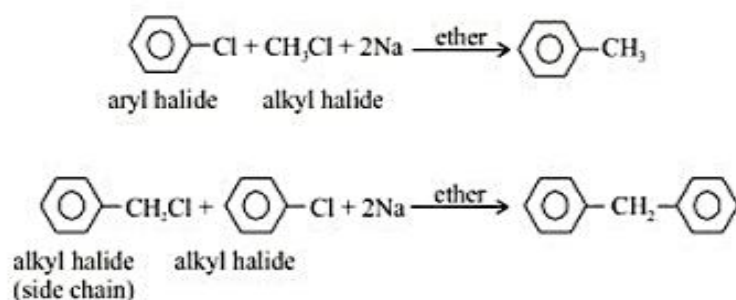




Substitution at the carbon (\*) that was attached to the leaving group is called direct substitution. Substitution at the adjacent carbon is called cine substitution.

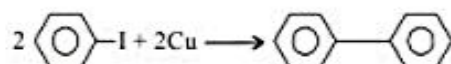


### (c) Wurtz-Fitting Reaction



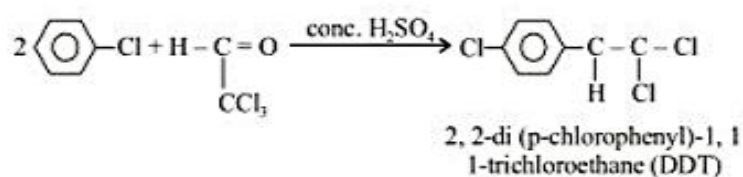
If only aryl halide is involved, diphenyl is formed (**Fitting reaction**)

### (d) Ullman synthesis



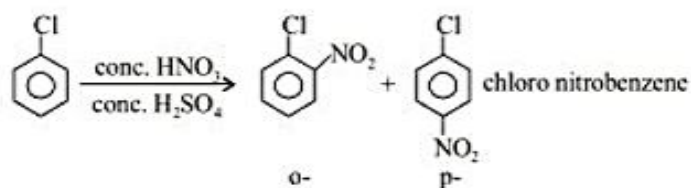
### (e) Reaction with Chloral

DDT is formed when chloral reacts with chlorobenzene in presence of concentrated  $\text{H}_2\text{SO}_4$ .

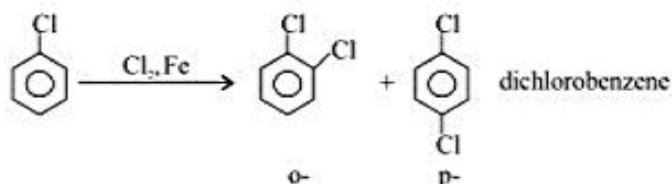


DDT is causing ecological problems, its use as insecticides is being banned.

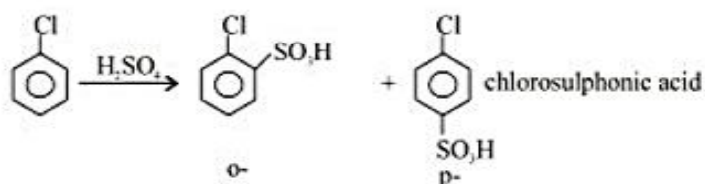
### Nitration



### Chlorination

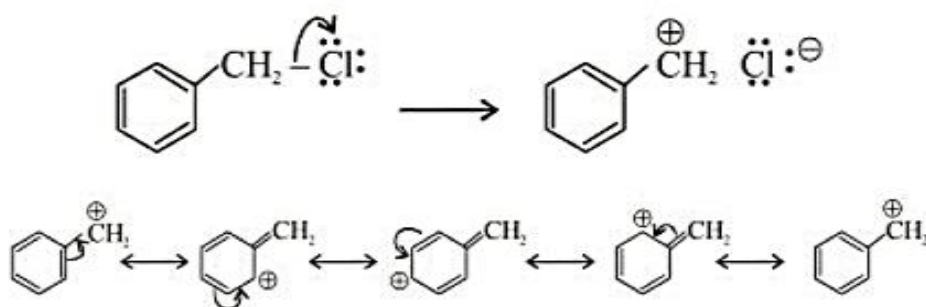


### Sulphonation

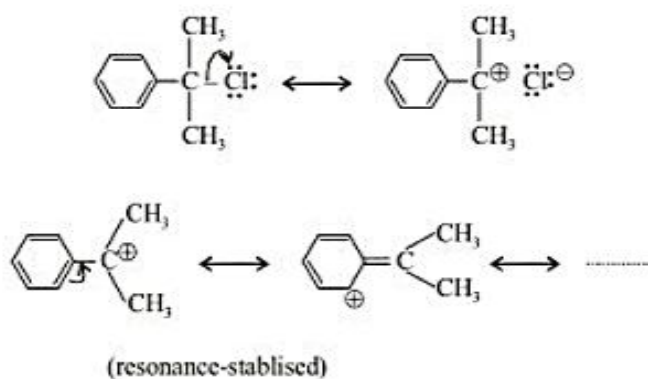


• Chlorine is not a good donor of electrons by resonance due to its high electronegativity. Thus, the inductive effect of the Cl atom overcomes the resonance effect, and thus, it deactivates the benzene ring.

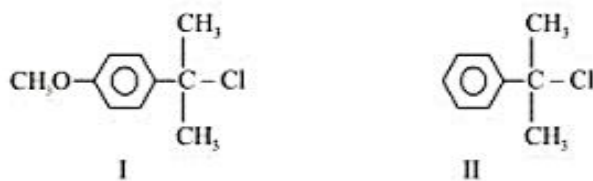
- (g) **Substitution on benzylic carbon ( $S_N$ ):** The greater reactivities of benzylic halides result from the stabilities of the carbocation intermediates that are formed when they react.



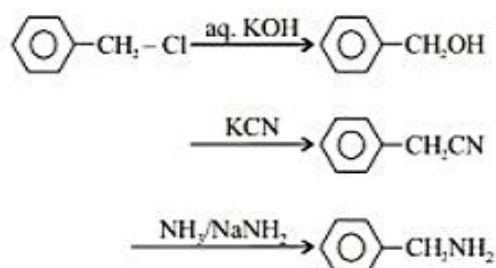
Tertiary cumyl chloride ionises to a carbocation with four important resonance structure :



Because of the possibility of resonance, ortho and para substituent group on the benzene ring that activate electrophilic aromatic substitution further accelerate  $S_N1$  reaction at the benzylic position. Thus p-methoxy tert-cumyl chloride (I) undergoes hydrolysis about 3400 times faster than tert-cumyl chloride II.

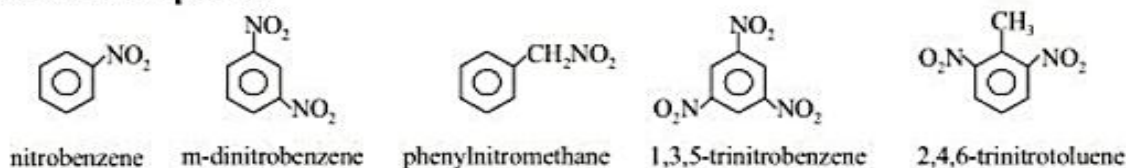


Benzylic halides undergo  $S_N$  reactions like aliphatic halides.



This provides a path of converting toluene into so many other compounds benzyl chloride.

### Aromatic Nitro Compounds



### Source

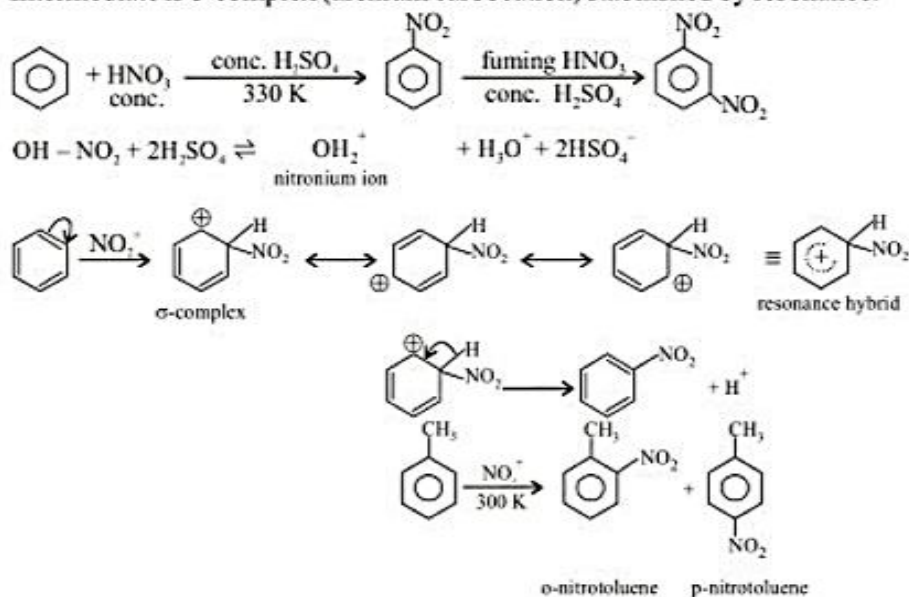
- Direct nitration

Nitrating agent is

(a) conc.  $\text{HNO}_3$  + conc.  $\text{H}_2\text{SO}_4$  or (b) acetyl nitrate ( $\text{N}_2\text{O}_5$  in acetic anhydride)

$-\text{NO}_2$  is deactivating group, hence, further nitration takes place with fuming  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  mixture.

Intermediate is o-complex (arenium carbocation) stabilised by resonance.

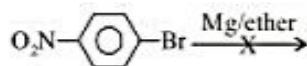




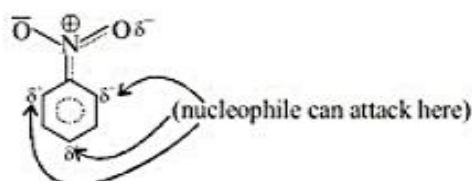
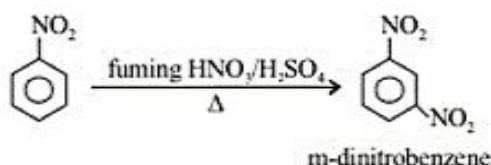


**Properties**

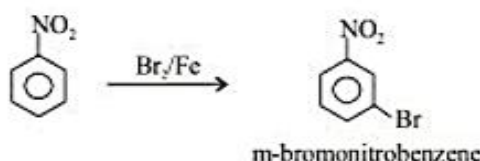
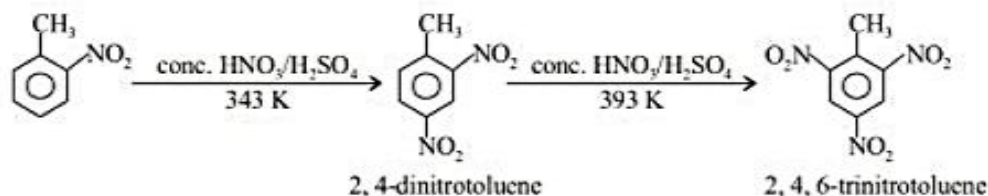
- Nitro-compounds are yellow crystalline solids (nitrobenzene is yellow liquid)
- Steam-volatile, denser than water in which they are insoluble.
- Nitro group is attacked by Grignard reagent; nitro-substituted aryl halides cannot be used for the preparation of these reagents.



There is also partial positive charge on the ortho and para-positions. Thus,  $-\text{NO}_2$  activates the benzene nucleus for nucleophilic substitution at the ortho and para-positions.

**Electrophilic substitution ( $\text{S}_\text{E}$ )**

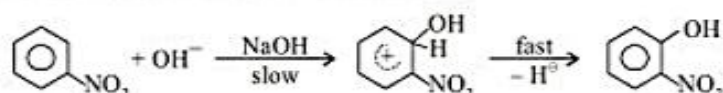
Further nitration to form trinitrobenzene takes place under drastic conditions. Presence of electron-releasing group activates benzene nucleus for  $\text{S}_\text{E}$ . Toluene can be nitrated only once but nitro group introduced retards a second nitration on the same ring.

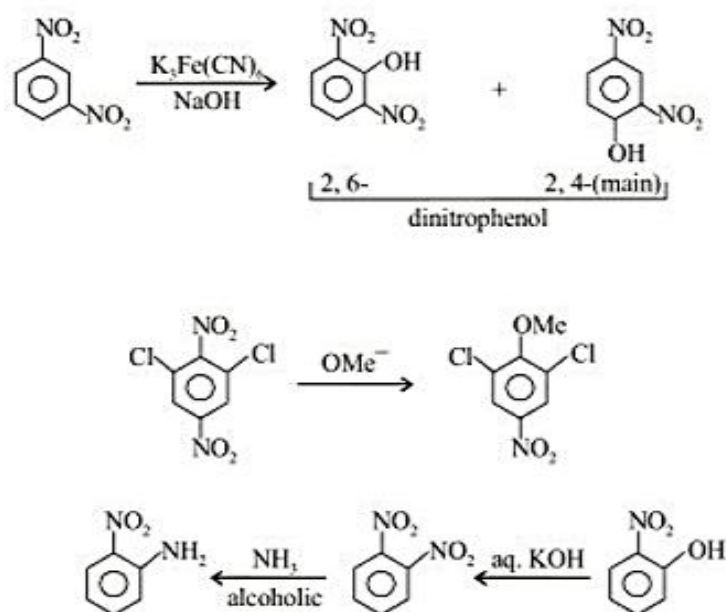


- $-\text{NO}_2$  group also deactivates benzene nucleus for alkylation by Friedel-Crafts reaction.

**NUCLEOPHILIC SUBSTITUTION REACTIONS**

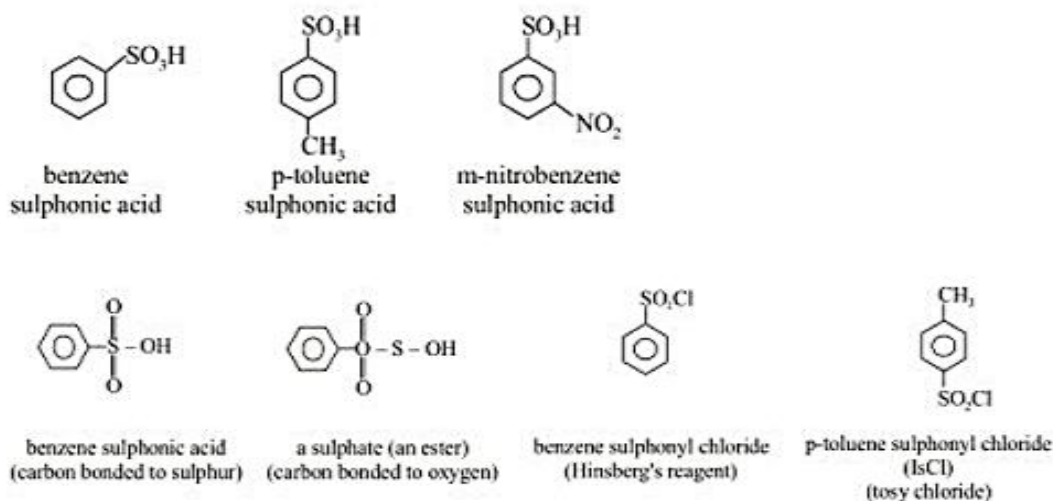
- Substitution of hydrogen by a nucleophile does not occur in benzene itself, but the presence of one nitro group is sufficient to activate the o- and p-positions.





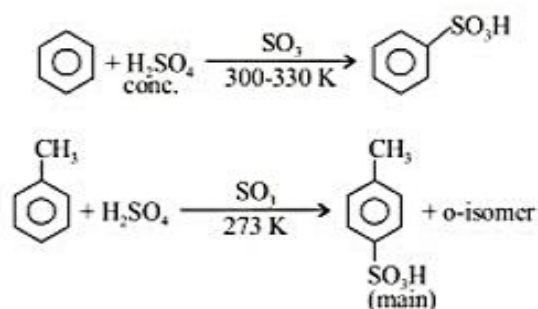
## AROMATIC SULPHONIC ACIDS

They are derivatives of aromatic hydrocarbons in which one or more hydrogen of the benzene ring have been replaced by the function  $-\text{SO}_3\text{H}$ , called the sulphonic group.



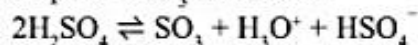
### Source

#### • Direct sulphonation :

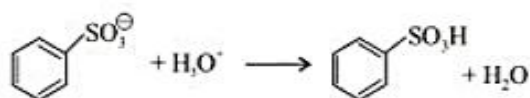
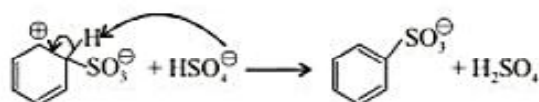
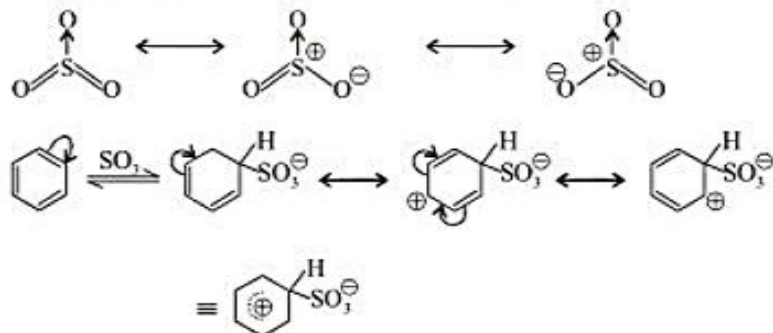




In the sulphonation, electrophile is  $\text{SO}_3$  formed as :



Although it appears neutral, sulphur carries positive charge due to resonance :

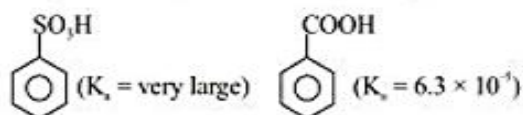


### Properties

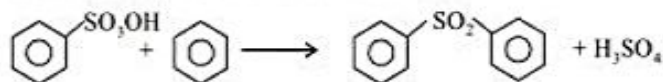
- Colourless crystalline deliquescent solid.
- Very soluble in water and solution is strongly acidic.



They are stronger acid than carboxylic acid.

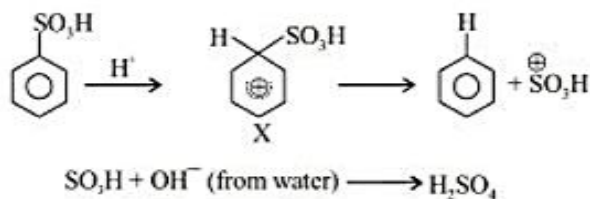


- **Formation of diphenyl sulphone :**



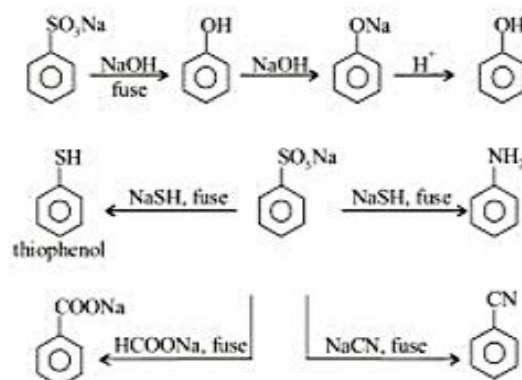
- **Desulphonation :**

The knocking out of sulphonic acid group from benzene nucleus is called **desulphonation**.



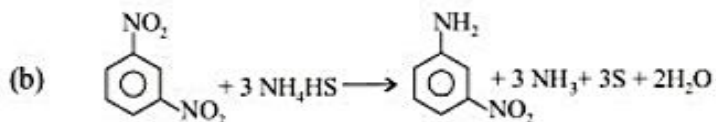
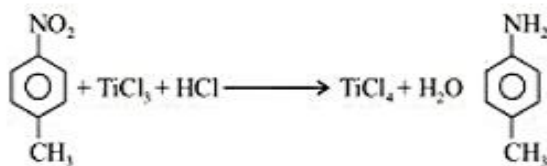
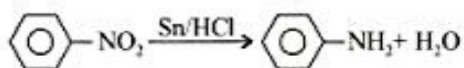
The desulphonation is very useful for preparation of certain isomers which are otherwise not obtained in pure state.

**Reactions of sodium salt of benzene sulphonic acid :**  
(conversion into other derivatives)

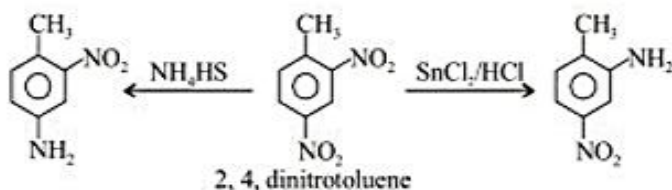


**Source**

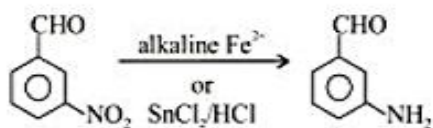
- (a) Nitrobenzene can be reduced under different media to produce aniline and related compounds.



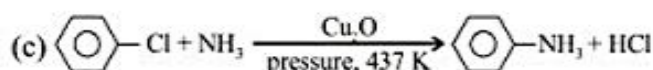
$\text{NH}_4\text{HS}$  is suitable reagent where only one  $-\text{NO}_2$  (in stages) is to be reduced.



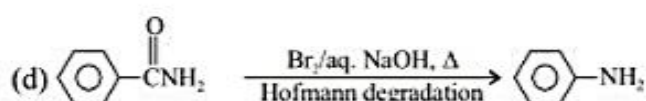
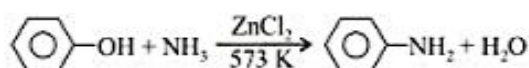
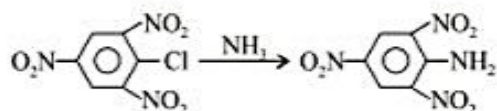
Action of  $\text{NH}_4\text{HS}$  and  $\text{SnCl}_2/\text{HCl}$  is specific.  $\text{NH}_4\text{HS}$  reduces  $-\text{NO}_2$  para to  $-\text{CH}_3$  while  $\text{SnCl}_2/\text{HCl}$  reduces  $-\text{NO}_2$  ortho to  $-\text{CH}_3$ .



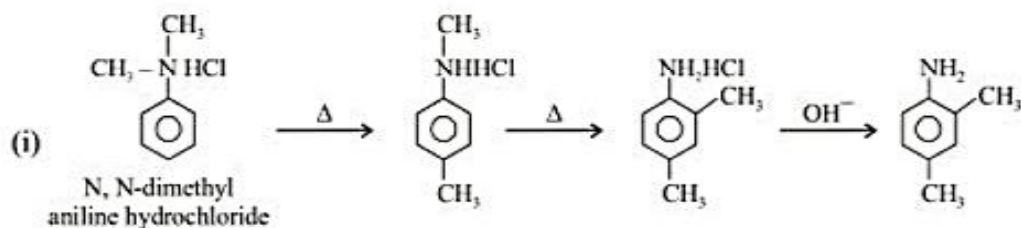
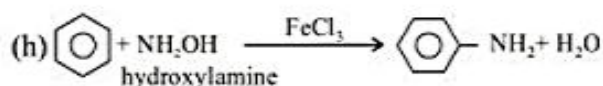
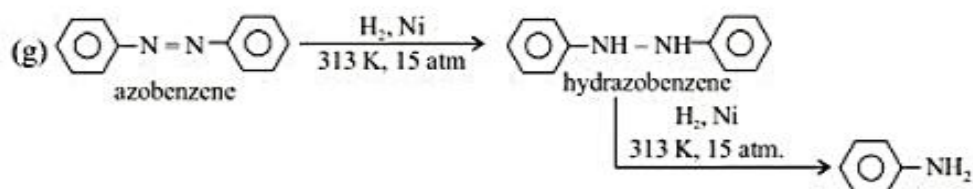
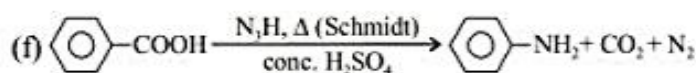
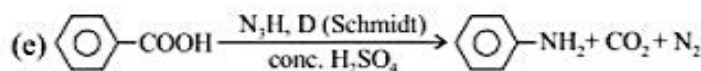
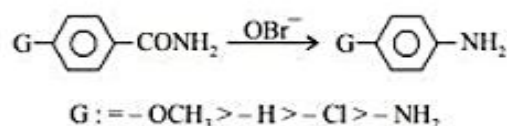
Alkaline  $\text{Fe}^{2+}$  does not reduce  $-\text{CHO}$  into  $-\text{CH}_2\text{OH}$ .  $\text{SnCl}_2/\text{HCl}$  can also be used here.



C–Cl bond is stable, hence ammonolysis of aryl halide takes place under high temperature and pressure. However electron withdrawing group in benzene nucleus makes C–Cl bond highly reactive.

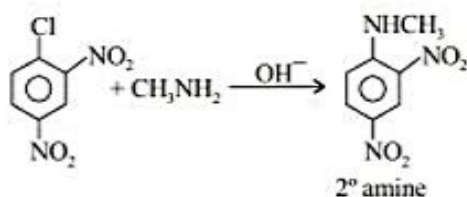
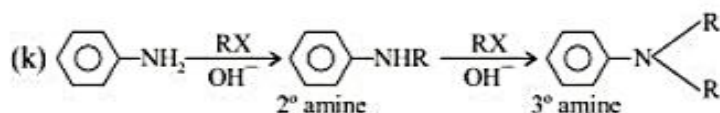
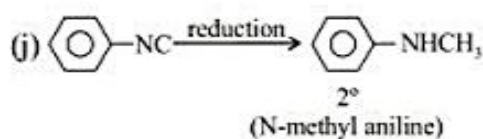


When the migrating group is aryl, the rate of the Hofmann degradation reaction is increased by the presence of electron releasing substituents in the aromatic ring.



This is called Hofmann-Martius rearrangement and alkyl group preferentially migrates to p-position and if it is occupied, then to o-position.



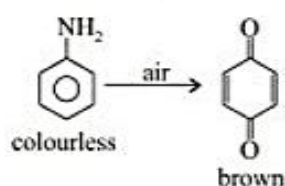


Some other methods are very similar to that used for aliphatic amines.

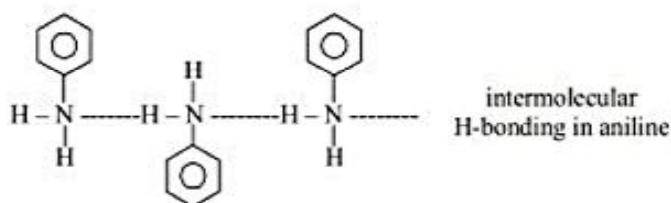
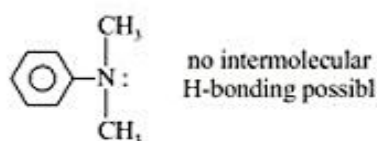
## Properties

### Physical

- Colourless liquid/solids, but due to air oxidation, they turn brown.



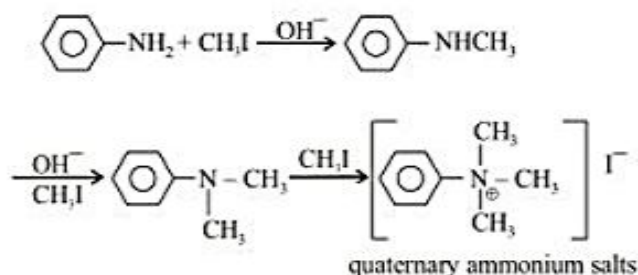
- Slightly soluble in water (polar solvent) but highly soluble in benzene and other organic solvents.
- High b.p. due to intermolecular H-bonding. N, N-dimethyl aniline has lower b.p. due to lack of H-bonding but molecular weight is also important affecting b.p.



- Para-substituted aniline, being the most symmetric, have the highest melting points. Thus p-toluidine is solid at room temperature while o-toluidines are liquids.

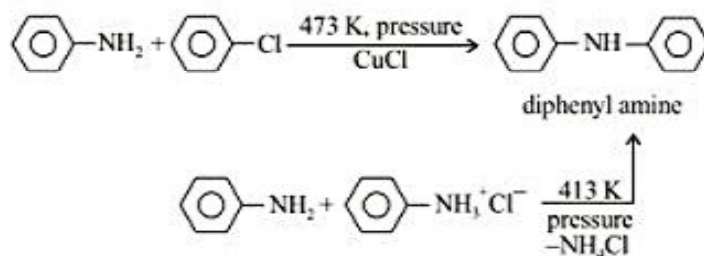
## Relations of the $-\text{NH}_2$ group

### (a) Methylation (Alkylation)

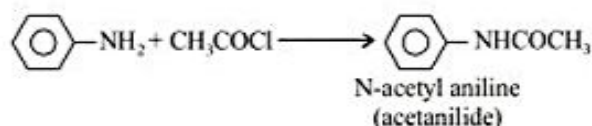


### (b) Arylation

Arylation of aniline with  $\text{C}_6\text{H}_5\text{Cl}$  is difficult.

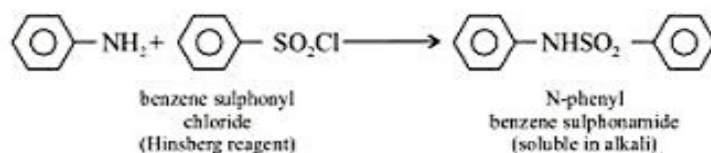


### (c) Acylation



Acetyl group deactivates  $-\text{NH}_2$  group, whenever aniline is subjected to nitration, acetylation is necessary to protect the ring from being oxidised.

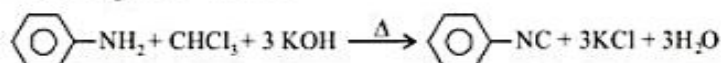
### (d) Sulphonylation

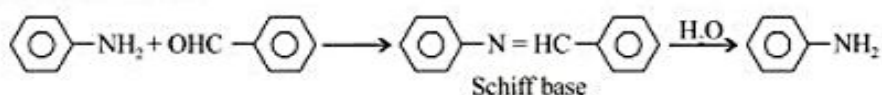


$2^\circ$  amine also reacts but the product is insoluble in alkali. This provides a method (called Hinsberg method) of separation of mixture of  $1^\circ$ ,  $2^\circ$  and  $3^\circ$  amines.

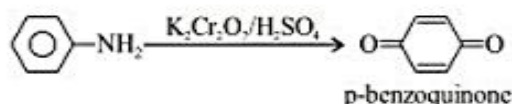
### (e) Carbylamine Reaction

Only  $1^\circ$  amines give this reaction when unpleasant smell of isocyanides is obtained on heating a mixture of alcoholic  $\text{KOH}$ ,  $\text{CHCl}_3$  and  $1^\circ$  amine.

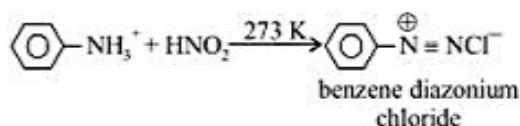
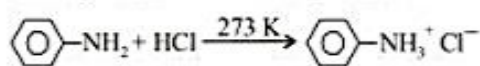
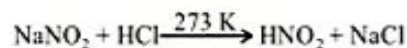


**(f) Formation of Schiff base**

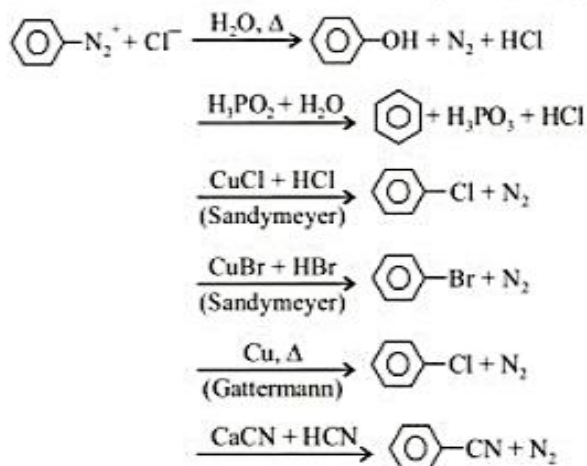
These Schiff bases are easily hydrolysed to the free amines and so their formation offers a mean of 'protecting' an amino group (during nitration).

**(g) Oxidation****(h) Reaction with  $\text{HNO}_2$** 

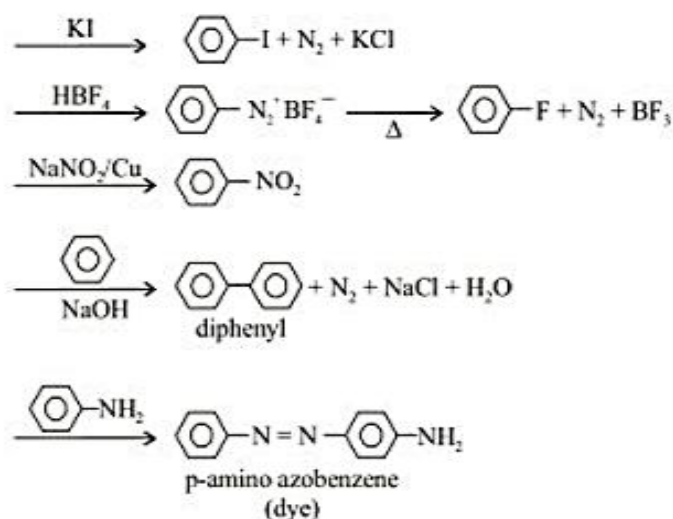
1° amines form diazonium salts at low temperature (273–278 K). A reaction in which  $-\text{NH}_2$  group is converted into diazo group ( $-\text{N}^{\oplus}=\text{N}$ ) is called diazotisation. Diazonium salts are stable in cold aqueous solution.



Aniline can be converted into so many other compounds through the formation of diazonium salts.

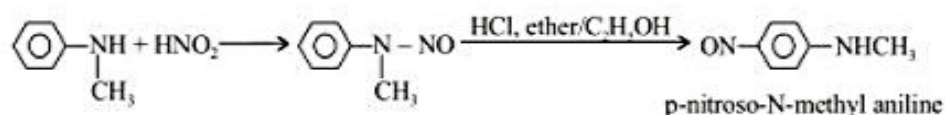




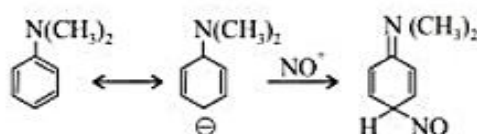


More reactions are given in sec. 16.8 (diazonium salts)

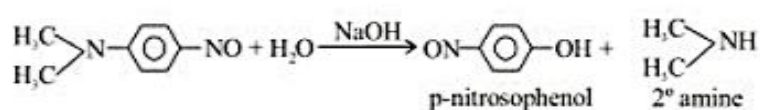
2° amines form nitrosamine (yellow oily liquid) which is stable at room temperature. However on reaction with HCl in ether and alcohol – NO group migrates to para-position (Fischer-Hepp)



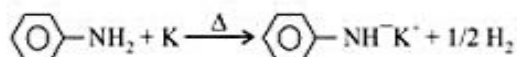
3° amines form p-nitroso derivatives :



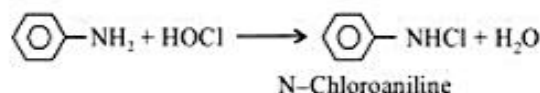
Hydrolysis of p-nitroso derivative gives 2° amines :



This provides a path of the preparation of 2° amines :

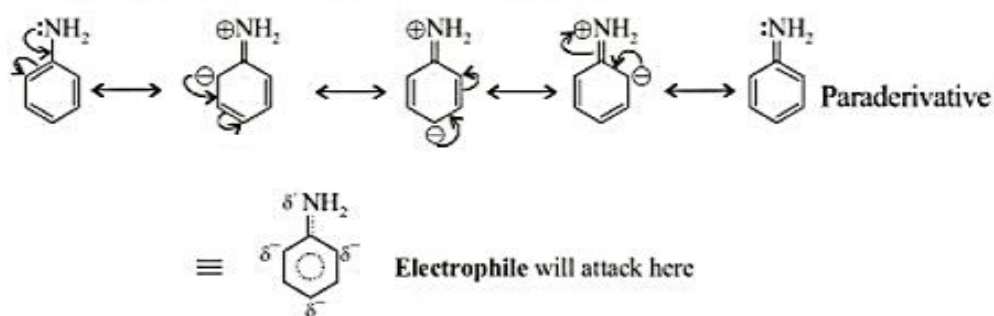


This represent acidic nature of aniline. Hypochlorous acid also reacts with aniline in which active H is replaced. :

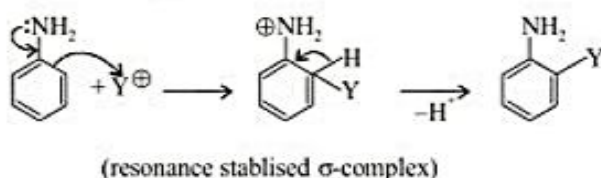


### Electrophilic substitution in benzene nucleus

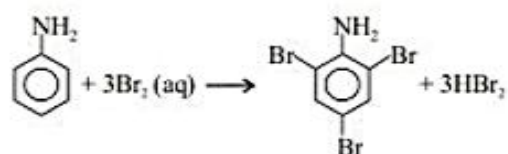
–NH<sub>2</sub> group is o, -p directing and activating group.



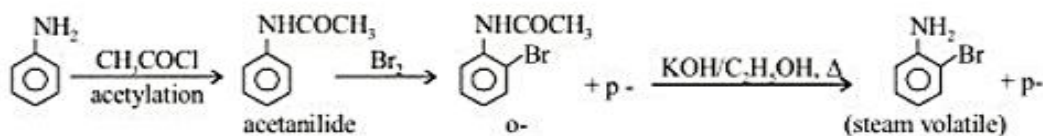
Hence, –NH<sub>2</sub> group activates benzene nucleus for ortho and para-electrophilic attack.



### (a) Bromination

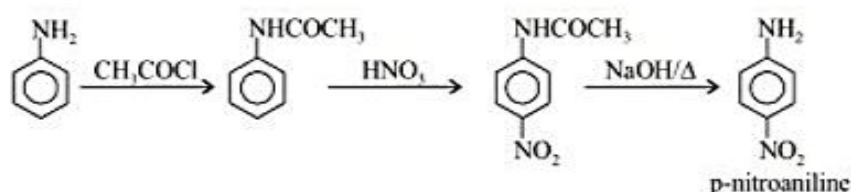
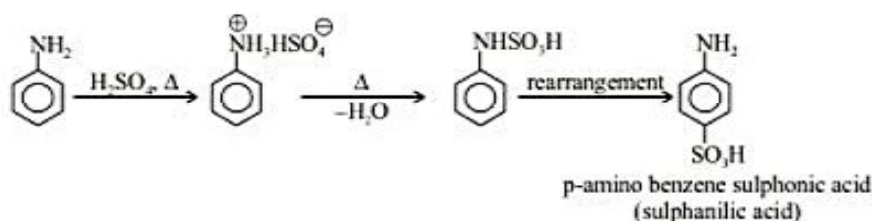


–NH<sub>2</sub> group is greatly activating group hence reaction takes place rapidly. However if ring is deactivated by acetylation, o- and p-isomers are obtained.

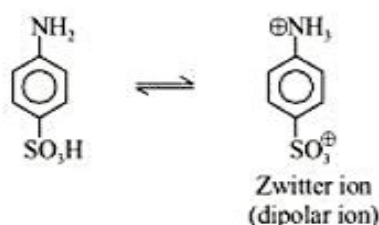


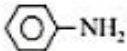
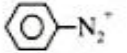
**(b) Nitration**

Direct nitration of aniline with nitric acid gives a complex mixture of mono-, di- and tri-nitro compounds and oxidation products. If  $-\text{NH}_2$  group is protected by acetylation and then nitrated, p-isomer is the main product.

**(c) Sulphonation**

Like antranilic acid, sulphanilic acid also exists as Zwitter ion due to internal neutralisation.

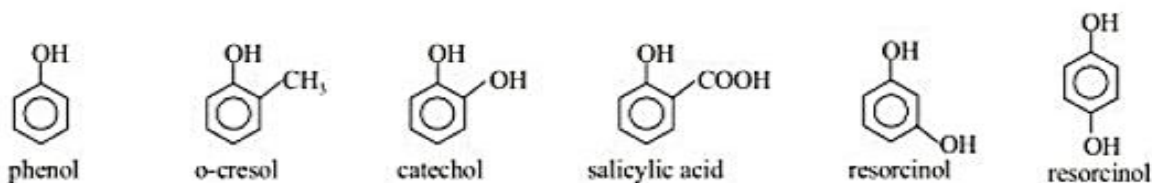
**Distinction between Aliphatic and Aromatic Amines**

S.No.	Test		$\text{CH}_3\text{NH}_2$
1.	Diazotisation (reaction with $\text{HNO}_2$ )	Diazonium salt is formed  which forms azo dye with phenolic compounds.	$-\text{NH}$ is replaced by $-\text{OH}$
2.	$\text{S}_\text{E}$	can be halogenated, sulphonated, nitrated.	no
3.	Basic nature	less basic than $\text{CH}_3\text{NH}_2$ , $\text{NH}_3$	more basic than $\text{NH}_3$



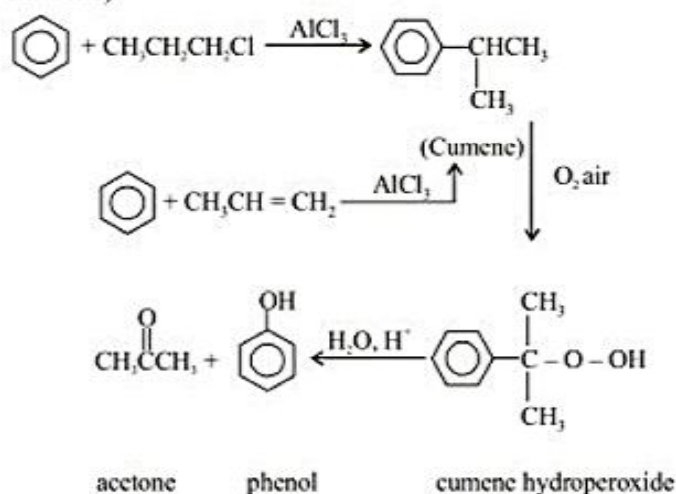
## Phenolic compounds

Phenols are the compounds of the general formula  $\text{ArOH}$ , where, Ar is phenyl or substituted phenyl. Phenols differs from alcohols in having the  $-\text{OH}$  group attached directly to an aromatic ring.

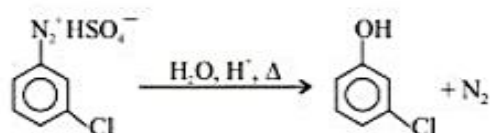


### Source

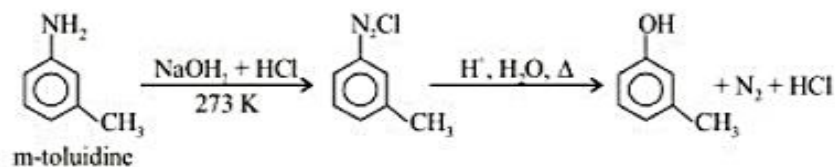
- From Cumene (Isopropyl benzene)



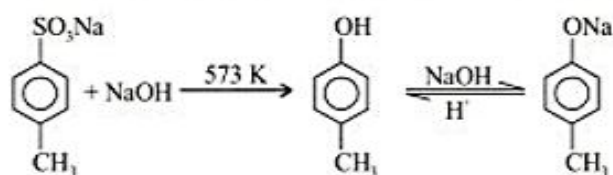
- Hydrolysis of Diazonium salts



Diazonium salts are obtained from aniline and its derivatives by a process called **diazotisation**.

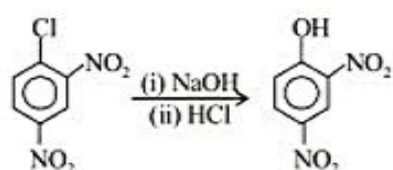
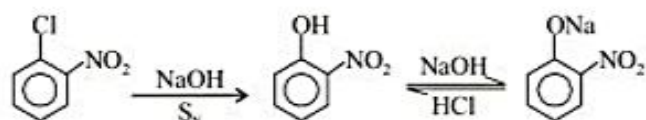
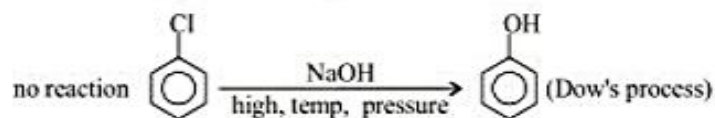


- Alkali Fusion of Benzene Sulphonic Acid salts

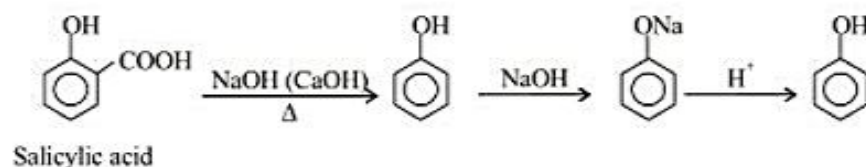


### • Hydrolysis of Aryl Halides

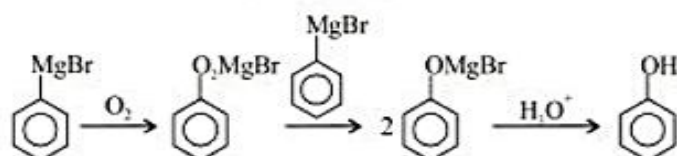
Halogen atom attached to benzene nucleus does not give  $S_N2$  reaction since C–X bond is stable due to resonance. However, in presence of electron withdrawing group in o- and p-positions,  $S_N$  reaction is favoured and phenolic compounds are formed.



### • Distillation of Phenolic Acids



### • Oxidation of Grignard Reagent



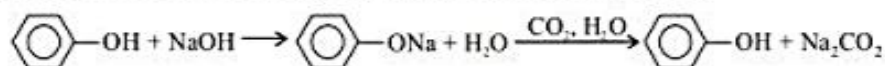
## MIDDLE OIL OF COAL-TAR DISTILLATION

Middle oil of coal-tar distillation has naphthalene and phenolic compounds. Phenolic compounds are isolated in following step :

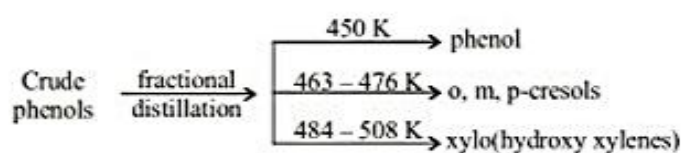
**Step-I :** Middle oil is washed with  $\text{H}_2\text{SO}_4$ . It dissolves basic impurities like pyridine (base).

**Step-II :** Excessive cooling separates naphthalene (a low melting solid)

**Step-III :** Filtrate of step II is treated with aqueous NaOH when phenols dissolves as phenoxides. Carbon dioxide is then blown through the solution to liberate phenols.



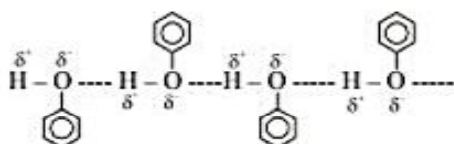
**Step-IV :** Crude phenol (of step III) is subjected to fractional distillation.



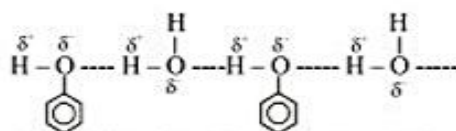
## Properties

### Physical

- Simplest phenols are liquids or low-melting solids.
- They are capable of forming intermolecular H-bonding among themselves and with water. Thus,
  - they have high b.p.
  - they are soluble in water.



(intermolecular H-bonding among phenol molecules)



(crossed intermolecular H-bonding between water and phenol molecules)

– due to intermolecular H-bonding and high dipole moment, m.p. and b.p. of phenol are much higher than that of hydrocarbon of comparable molecular weights.

Solute	mol. wt.	b.p.	m.p.
phenol	94 g mol <sup>-1</sup>	455 K	314 K
toulene	92 g mol <sup>-1</sup>	384 K	178 K

### Comparison of properties of nitrophenols

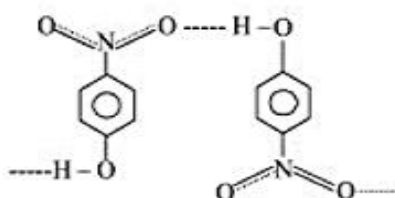
Isomer	b.p. at 760 mm	Solubility g/100 g	
o-nitrophenol	373 K	0.2	volatile in steam
p-nitrophenol	decomposes	1.69	non-volatile in steam
m-nitrophenol	467 K	1.35	non-volatile in steam

From the above table, it is clear that o-nitrophenol has much lower b.p. and much lower solubility in water than its isomer and is only steam-volatile.

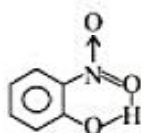
– m and p-isomer have high b.p. because of intermolecular H-bonding and high solubility in water is again due to crossed intermolecular H-bonding with H<sub>2</sub>O.

o-isomer has intramolecular H-bonding due to which association with different molecules decreases hence, b.p. is low giving volatile character to it and also H-bonding with  $\text{H}_2\text{O}$  molecules is not possible which makes it water soluble to a very small extent.

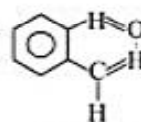
– Steam distillation depends upon a substance having an appreciable vapour pressure at the b.p. of water, by lowering the v.p., intermolecular hydrogen bonding inhibits steam distillation of the m-and p-isomer.



intermolecular hydrogen bonding in p-nitrophenol molecules

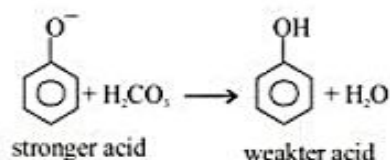
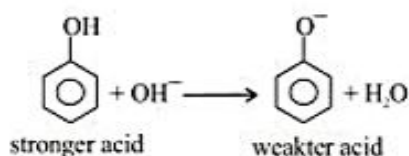


intramolecular hydrogen bonding in o-nitrophenol (chelation)

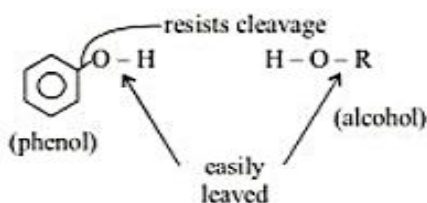


chelation in o-hydroxybenzaldehyde

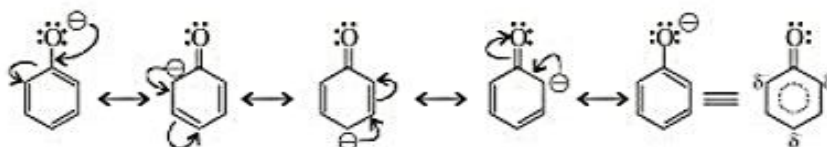
## ACIDITY OF PHENOLS AND EFFECT OF SUBSTITUENTS ON IT



Phenols are converted into their salts by aqueous  $\text{NaOH}$ , but not by aqueous bicarbonates. The salts are converted to free phenols by aqueous mineral acids ( $\text{HCl}$ , etc.), carboxylic acid or carbonic acids. Phenol is more acidic than alcohols but less than carboxylic acid. Enhanced acidity of phenol is due to (a) polar effect (b) resonance effect.

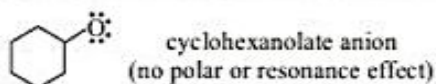


$\text{C}_6\text{H}_5$  - (phenyl) group is electron-withdrawing and phenoxide ion is more resonance stabilised than phenol, hence following equilibrium is displaced towards the right where stable phenoxide ion is formed.

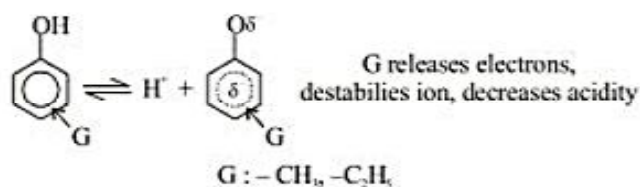
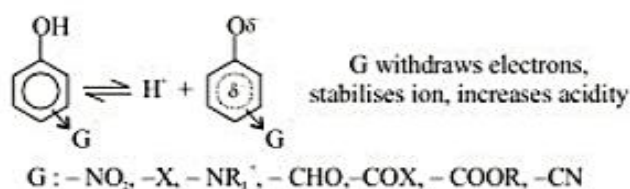




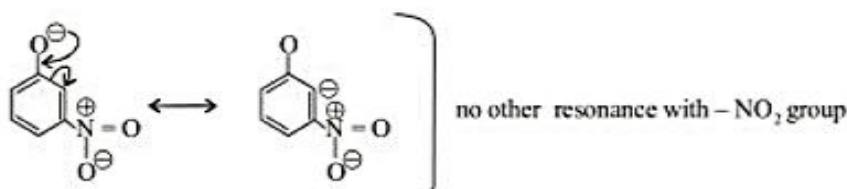
Alkoxides are stabilised neither by resonance nor by the polar effect of benzene rings or double bonds.



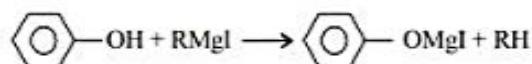
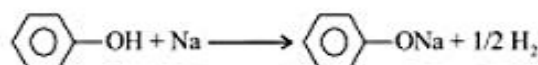
• Electron-attracting substituents like  $-X$ , or  $-\text{NO}_2$  increase the acidity of phenols and electron-releasing substituents like  $-\text{CH}_3$  decrease acidity.



$K_a$  (acidity constant) and  $\text{p}K_a$  of different substituted phenols are given in table. The marked lower acidity in case of meta-isomer is explained by the fact that m-nitrophenoxide ion is stabilised by inductive effect only and no resonance effect operates with  $-\text{NO}_2$  group.

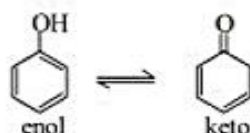


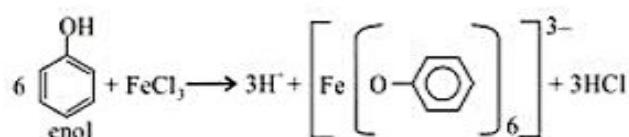
• Reactions in which phenol is a source of active H are :



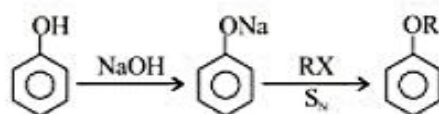
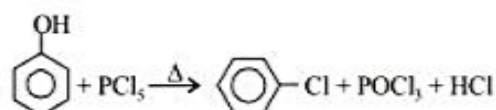
## FORMATION OF COMPLEXES WITH $\text{FeCl}_3$

Phenols form coloured iron complexes when related with neutral  $\text{FeCl}_3$  solution. The formation of iron complexes is attributed to the existence of keto-enol tautomerism in phenols. Phenol predominantly exists in enolic form, hence colour formation is used to identify phenols.

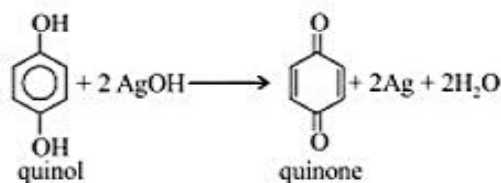
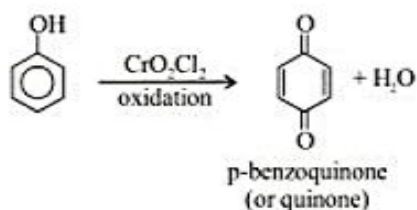
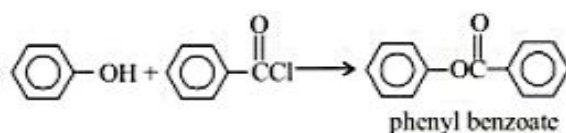
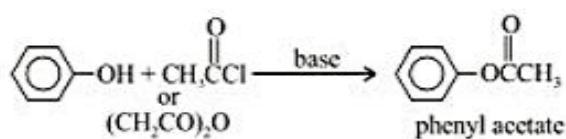
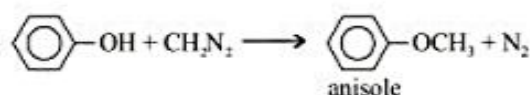




### Other Reaction of -OH Groups

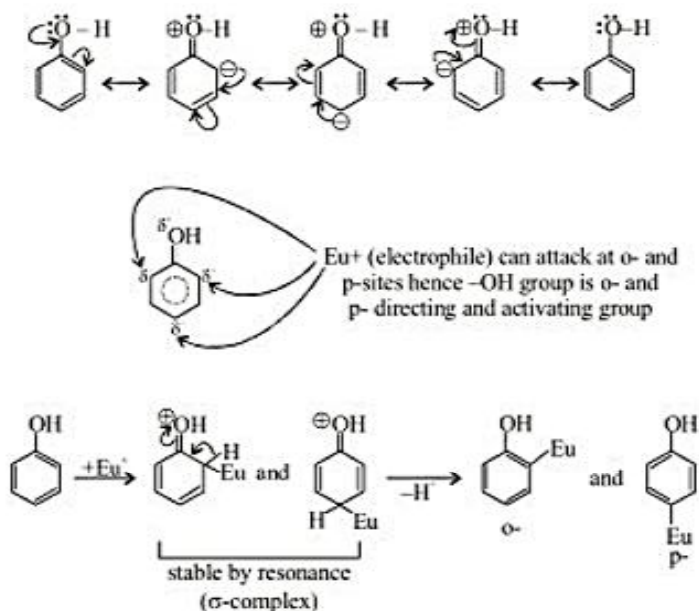


This is called Williamson's synthesis. The phenoxide ion is a nucleophile and will replace halogen of the alkyl halide.



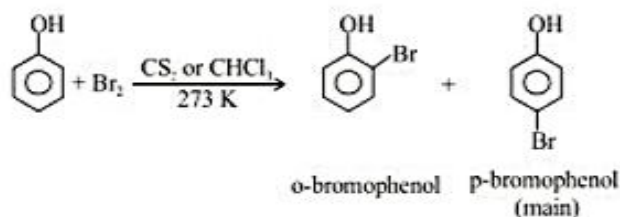
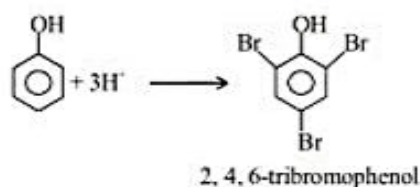
## ELECTROPHILIC SUBSTITUTION IN BENZENE NUCLEUS

–OH group is o- and p-directing and activating group for SE reactions.

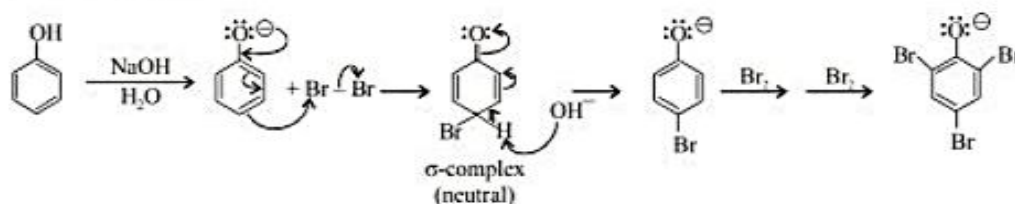


## HALOGENATION

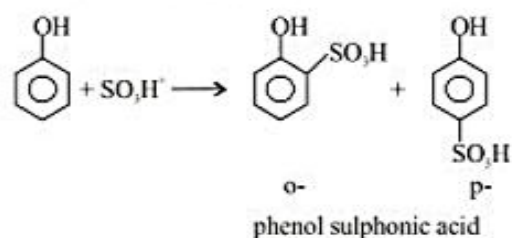
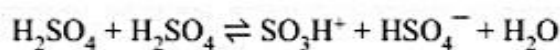
With excess of Br<sub>2</sub> solution :



In presence of NaOH, phenoxide ion is formed which is more reactive than phenol towards electrophilic aromatic substitution.



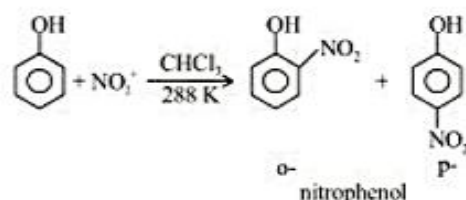
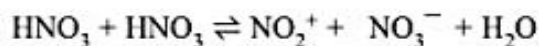
• **Sulphonation**



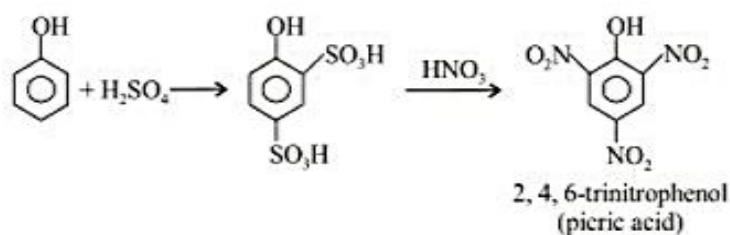
At room temperature, ortho-isomer while at 373 K the para-isomer is the main product.

• **Nitration**

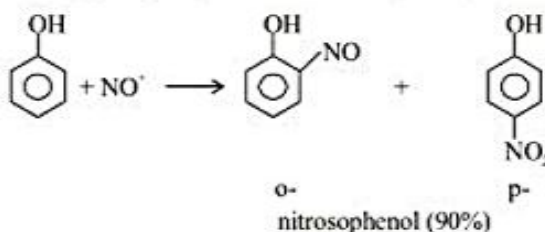
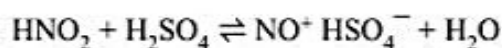
–OH group is activating group, hence, nitration is possible with dil.  $\text{HNO}_3$ .



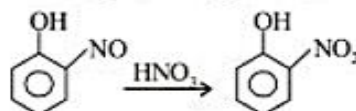
$\text{HNO}_3$  is oxidising agent and may lead to cleavage of benzene ring hence, further nitration is done carefully. However ring can be deactivated by sulphonation and then nitration will give picric acid in better yield.



• **Nitrosation**

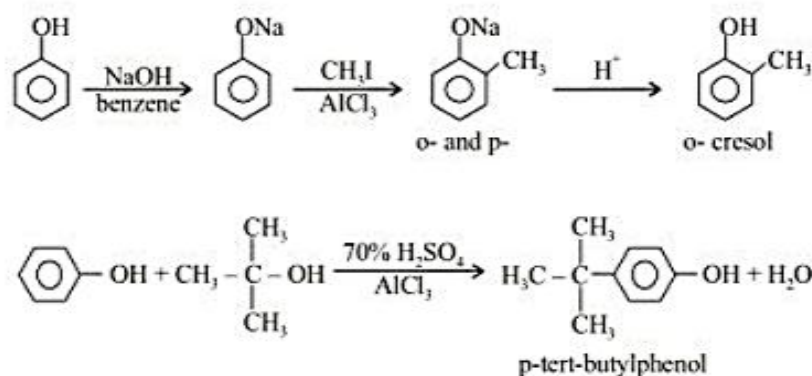


Nitrosophenol can be oxidised to  $-\text{NO}_2$  by  $\text{HNO}_3$ ; this provides a path of preparing nitrophenol.

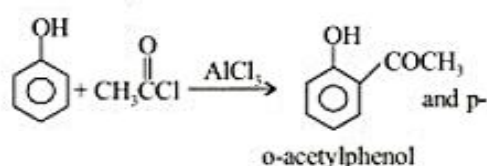




### • Alkylation (Friedel-Crafts Reaction)



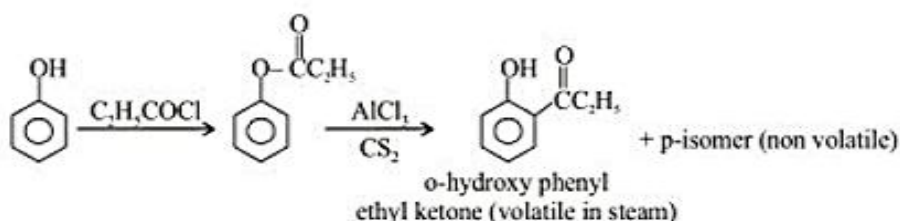
### • Acylation (Friedel-Crafts Reaction)



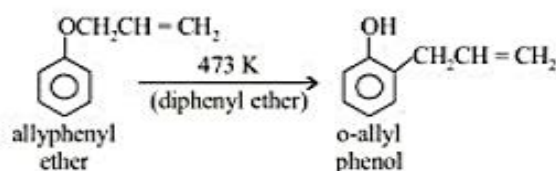
Intermediate of this reaction is  $\text{CH}_3\text{C}^+\text{=O}$  (acylium ion).

### • Fries rearrangement

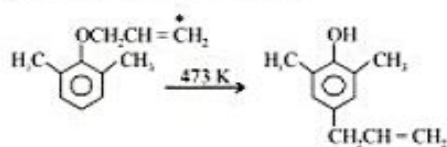
When esters or phenols are heated with  $\text{AlCl}_3$ , the acyl group migrates from the phenolic oxygen to an ortho or para-position of the ring thus, yielding a ketone. This reaction is called the Fries rearrangement and appears to involve generation of an acylium ion,  $\text{RCO}^+$ , which then attack the ring as in ordinary Friedel-Crafts acylation.



### • Claisen rearrangement



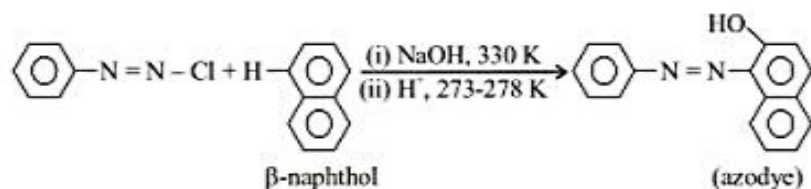
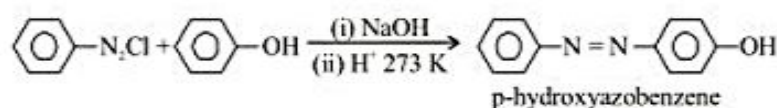
This is the arrangement of allyl ethers to allyl phenols. Allyl group migrates to ortho-position. If ortho-position is already occupied, para-isomer is obtained.



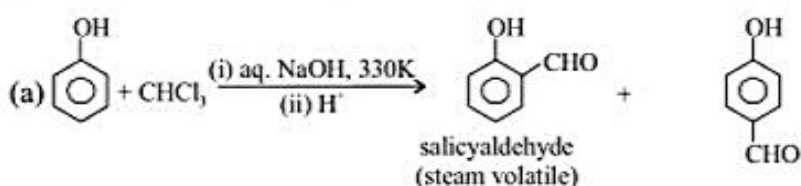
In this Claisen rearrangement, carbon which gets attached to benzene nucleus is vinylic and not allylic.

### • Coupling reactions (Azo dye formation)

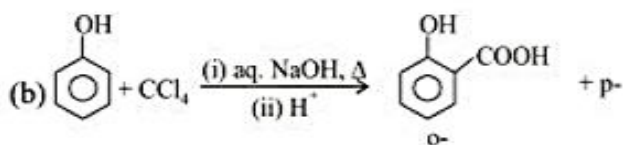
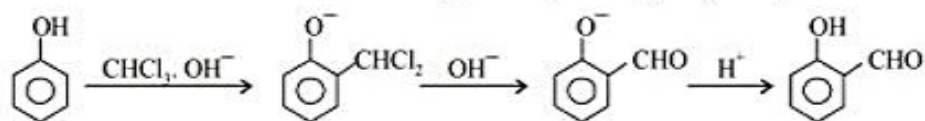
Phenol reacts with aryl diazonium salts in presence of alkali at low temperature to form form azo dyes.



### • Reimer-Tiemann Reaction

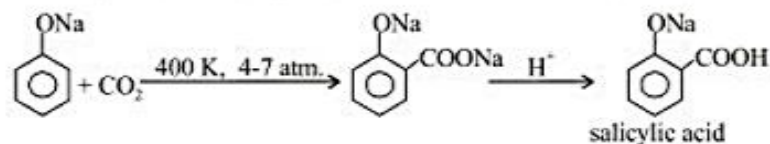


A substituted benzal chloride is initially formed, but is hydrolysed by the alkaline medium.

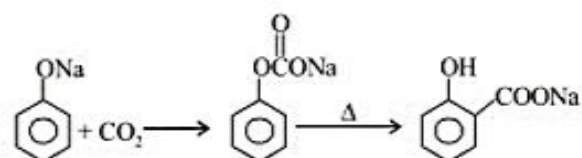


### • Kolbe reaction (Carbonation)

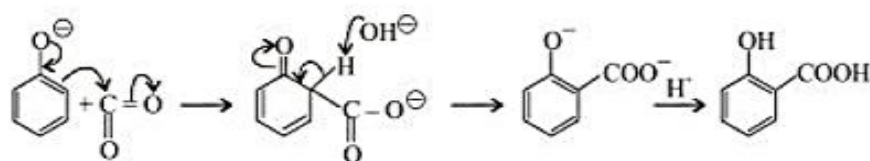
Treatment of the salt of a phenol with  $\text{CO}_2$  under pressure brings about substitution of the carboxyl group,  $-\text{COOH}$ , for hydrogen of the ring. This is called Kolbe reaction.



This provides a path of conversion of phenol into hydroxy carboxylic acids. It seems likely that  $\text{CO}_2$  attaches itself initially to phenoxide oxygen rather than to the ring.

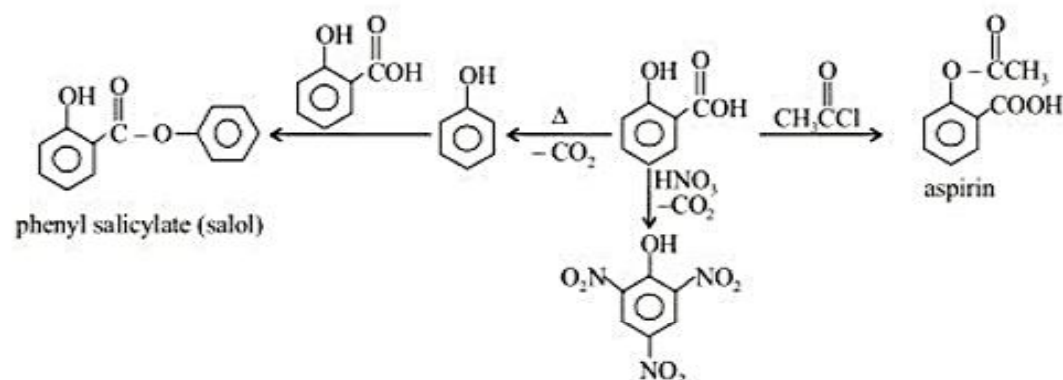


At high temperature (525 – 575 K), p-isomers is obtained.

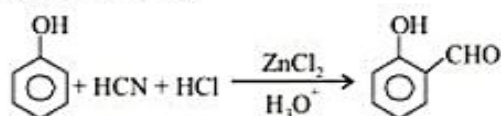


H-atom attached to the ortho-position combines with phenoxide oxygen.

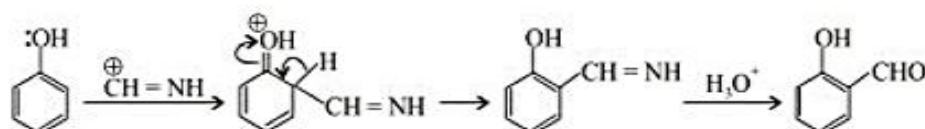
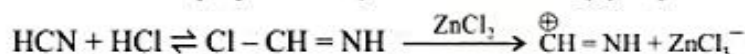
Salicylic acid is used to prepare aspirin, salol and picric acid :



#### • Gattermann Reaction (Formylation)

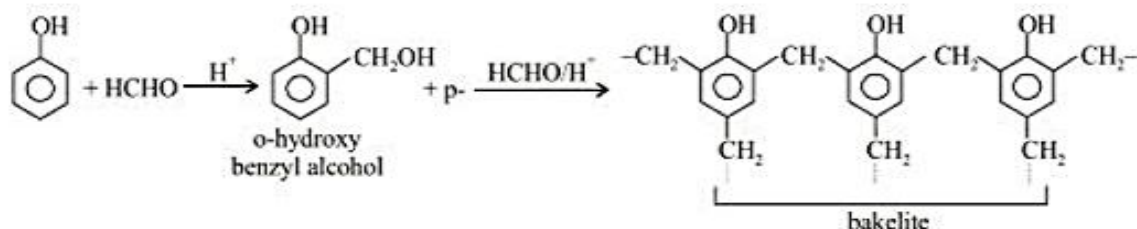


This reaction is used to prepare aldehyde when activating groups like  $-\text{OH}$ ,  $-\text{NH}_2$  are present.

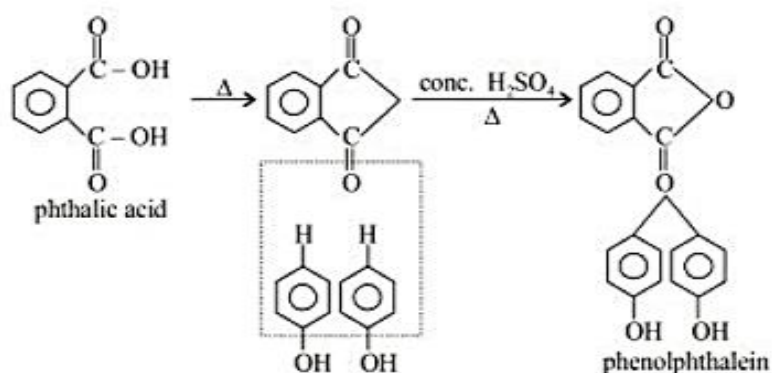


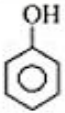
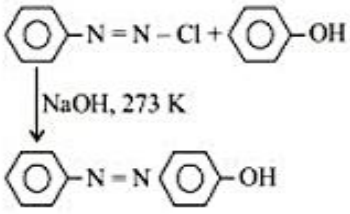
#### • Condensation Reaction

(a) Condensation of phenol with  $\text{HCHO}$  in presence of acid forms bakelite.



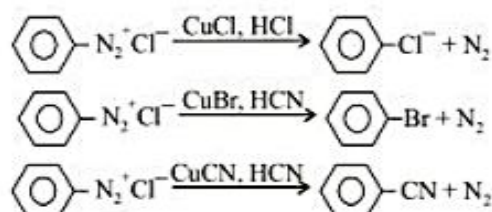
(b) Condensation of phenol with phthalic acid in presence of concentration  $\text{H}_2\text{SO}_4$  forms phenolphthalein (an indicator) which gives pink colour with  $\text{NaOH}$  (phthalein test of dibasic acid)



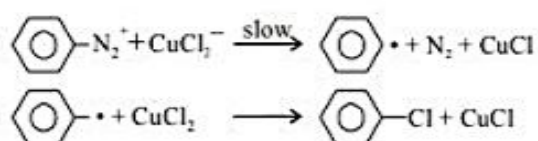
S.No.	Test		$\text{CH}_3\text{CH}_2\text{OH}$
1. 2.	Neutral $\text{FeCl}_3$ Azo dye test	violet colour with benzene diazonium chloride is formed  	no reaction no dye formation
3. 4. 5.	Phthalein test Litmus test Iodoform test	is given turns blue not given	no given no change is given

• **Sandmeyer Reaction**

Nucleophiles such as  $\text{CN}^-$ ,  $\text{Cl}^-$  etc., replace the diazonium group if appropriate cuprous salt is added to the solution containing diazonium salt.

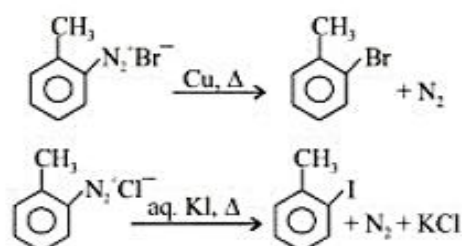


Sandmeyer reaction involves :  $\text{CuCl} + \text{Cl}^- \rightarrow \text{CuCl}_2^-$

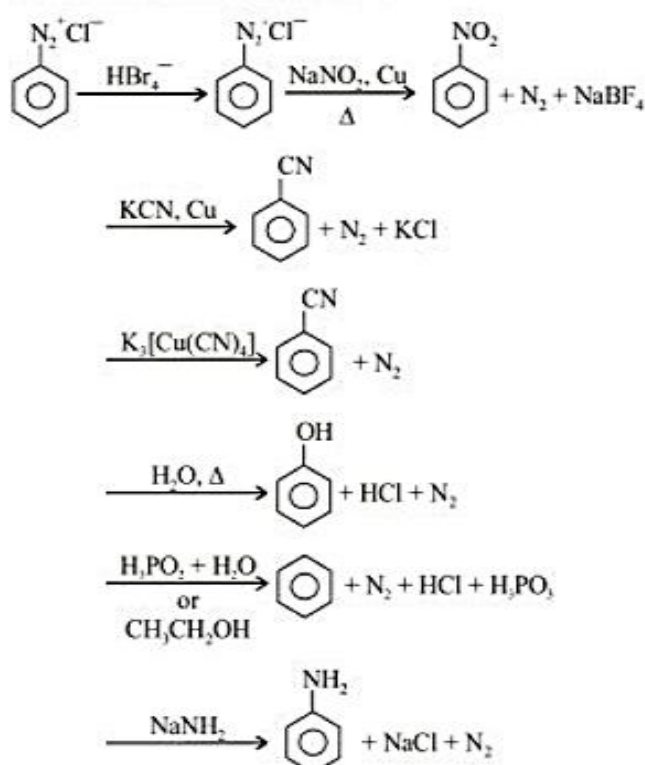




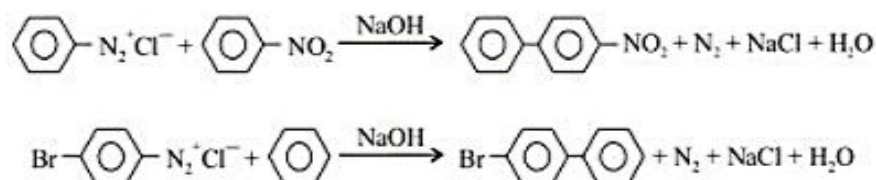
- Gattermann Reaction**



- Other Replacement Reactions**



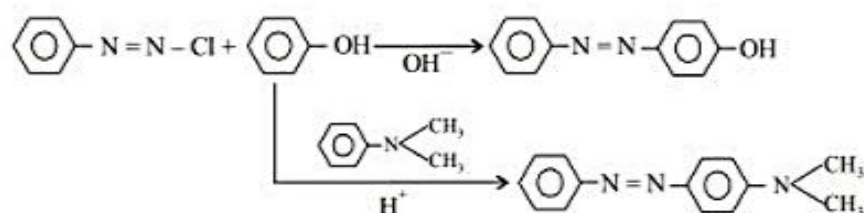
- Gomberg Reaction**



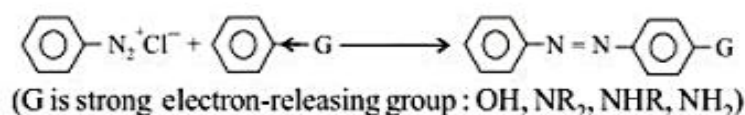
- Coupling reaction**

Diazonium salts undergo coupling reactions with phenols, naphthols and aromatic amines to form highly coloured azo-compounds.

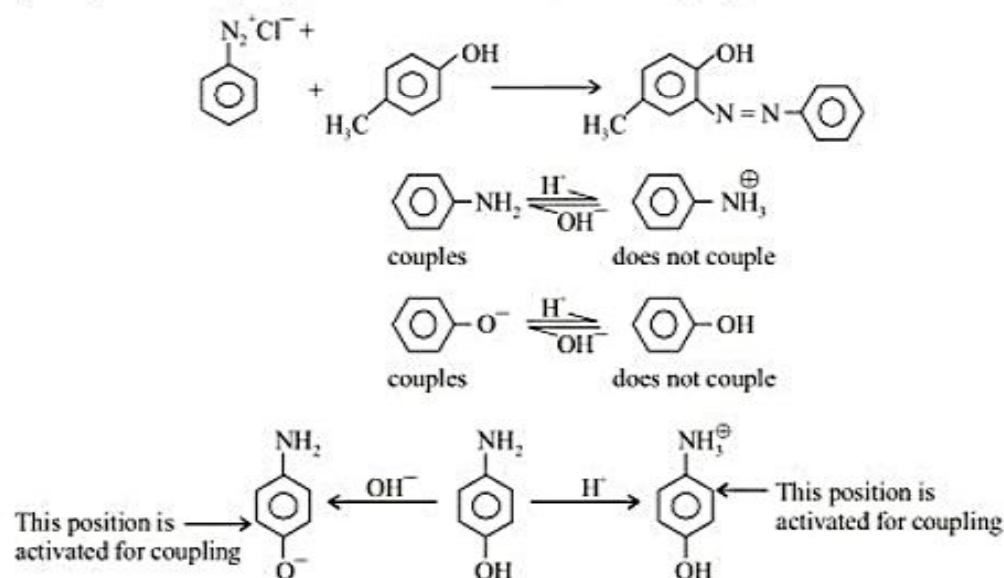
Arene diazonium ions act as weak electrophiles in (aromatic) electrophilic substitution. The products have the structure  $\text{Ar}-\text{N}=\text{N}-\text{Ar}$ , containing the  $-\text{N}=\text{N}-$  azo linkage. Thus products are called azo compounds and the reaction is called diazo coupling. Because diazonium salts are weak electrophiles, they react only with strongly activated ring (such as phenol, aniline).



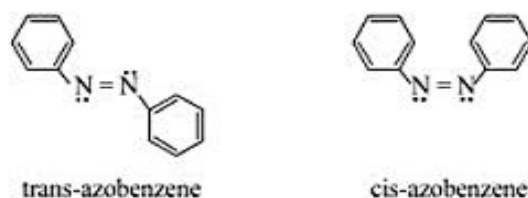
**In general :**



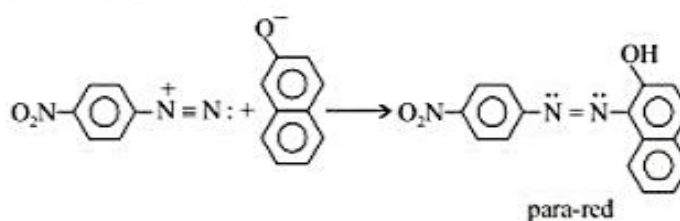
Coupling with benzene substrates occurs preferentially at the less sterically hindered p-position to the hydroxy or amino group, but if this is blocked, then o-coupling occurs.

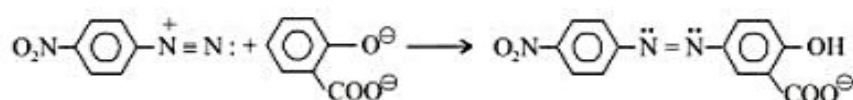


Azo compounds, like alkenes, can exist in cis and trans forms and because of steric strain, the trans-isomer is more stable than cis-isomer.



Azo compounds bring two substituted aromatic rings into conjugation with an azo group, which is a strong chromophore (a functional group absorption of light/colour). Thus most azo compounds are strongly coloured and they make dyes.

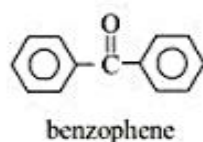
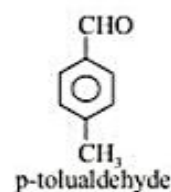
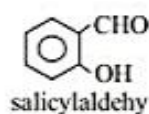
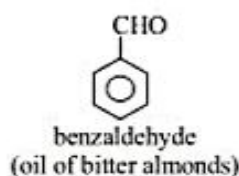




alizarin yellow

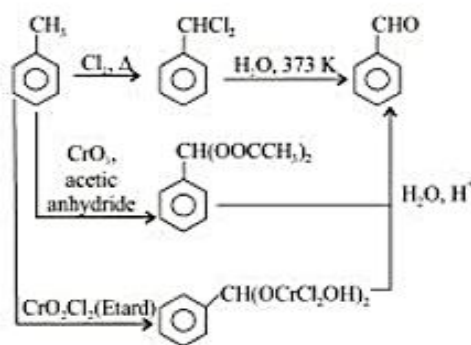
Diazo coupling often takes place in basic solutions since due to deprotonation of the phenolic –OH group or benzene sulphonic acid and carboxylic groups, activate the aromatic ring for  $S_E$  reaction. Common azo dyes have sulphonate/carboxylate groups to enhance solubility of the azo dye in water and to help bind the dye to the polar surface of common fibres such as cotton and wool.

## CARBONYL COMPOUNDS

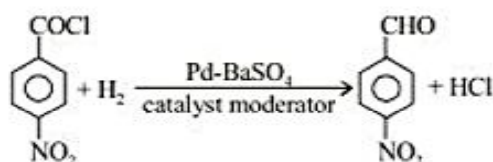


### Source

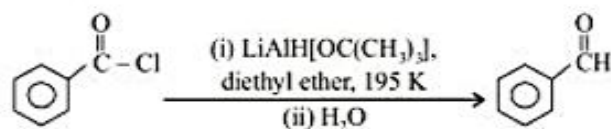
- From Toluene



### Rosenmund Reaction

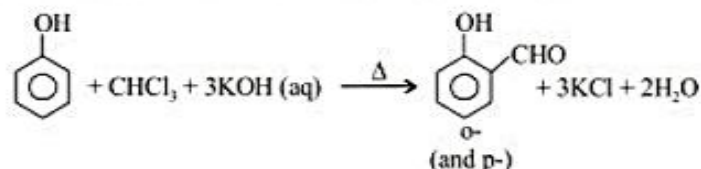


- Acyl chlorides can be reduced to aldehyde by treating them with lithium tri-ter-butoxy aluminium hydride,  $\text{LiAlH}(\text{OC}(\text{CH}_3)_3)_3$ , at 195 K.

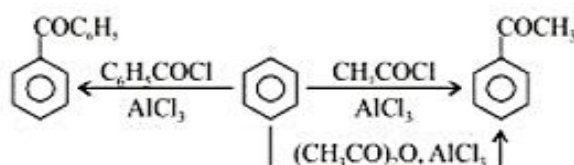


The reduction is brought by the transfer of a hydride ion from the aluminum atom to the carbonyl carbon of the acyl chloride. Subsequent hydrolysis frees the aldehyde.

- Reimer-Tiemann reaction is used to prepare phenolic aldehydes

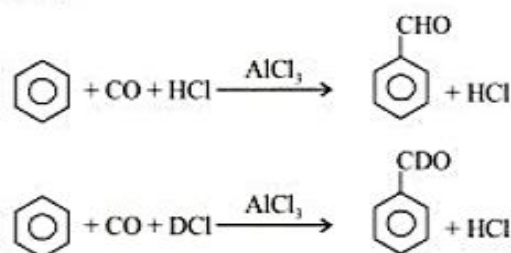


- Friedel-Crafts Acylation**



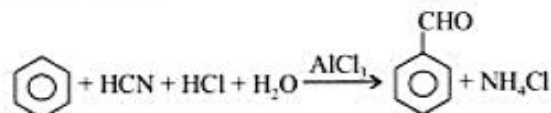
This reaction cannot be used on strongly deactivated aromatic systems.

### Gattermann-Koch Reaction

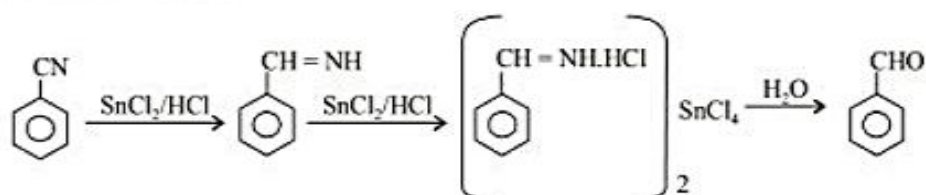


Thus, HCl (reactant) and HCl (product) are different. H of HCl (reactant) and CO appear in the form of -CHO in the benzene nucleus. It is confirmed by the fact that using isotopic DCI instead of HCl, would form -CDO and not -CHO. This reaction also succeeds only with benzene and activated benzene derivative.

- Gattermann-Aldehyde Synthesis**

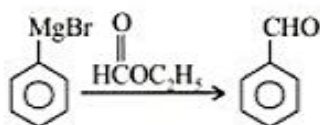


- Stephan Reaction**

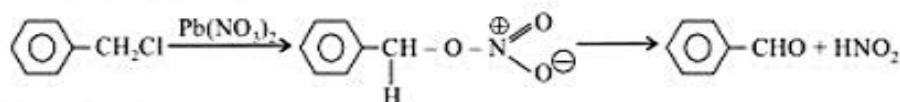




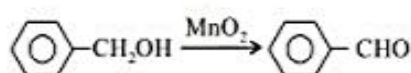
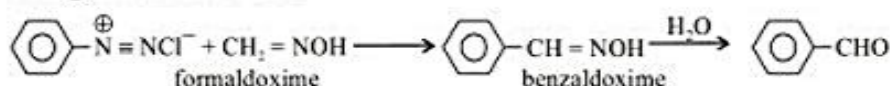
• **Grignard Reagent**



• **Oxidation of Benzyl Chloride**



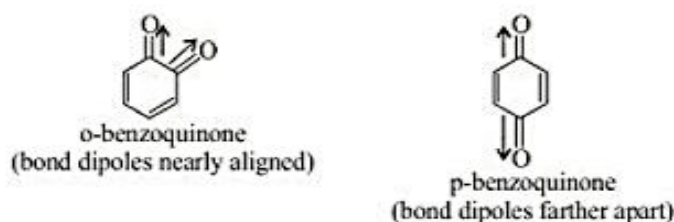
• **Using Diazonium Salts**



**Properties**

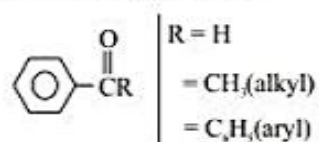
**Physical**

- $\text{C}_6\text{H}_5\text{CHO}$  is a colourless liquid with smell of bitter almond, sparingly soluble in water but readily in ethanol and ether.
  - $\text{C}_6\text{H}_5\text{COCH}_3$  is crystalline solid and is steam volatile; soluble readily in ethanol and ether but sparingly soluble in water. It produces natural type of sleep when administered orally.
- Ortho-quinones, particularly ortho-benzoquinone are less stable than their para-quinone isomers. It is due to the fact that in ortho-isomer, the  $\text{C}=\text{O}$  bond dipoles are nearly aligned and these have a repulsive destabilising interaction. In para-isomers, these dipoles are farther apart.



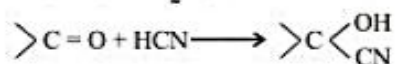
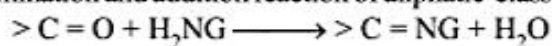
**Chemical**

Aromatic carbonyl compounds with following structure

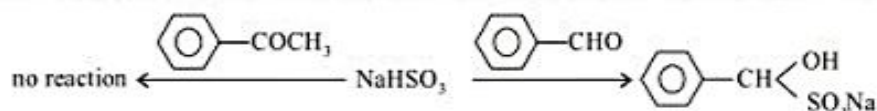


- Conjugation of the carbonyl carbon with the aryl ring reduces the electrophilic reactivity of the carbonyl carbon atom due to delocalisation of  $\pi$ -electrons. Hence, aromatic aldehydes and ketones are less reactive than aliphatic classes.
- Benzaldehyde, like aliphatic aldehydes, reduces Tollen's reagent (silver-mirror test). However, it does not reduce Fehling's solution. (a distinction from aliphatic class).

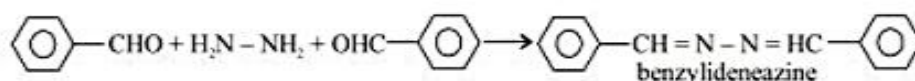
- They show elimination and addition reaction of aliphatic classes.



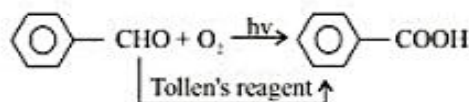
However, acetophenone does not form bisulphite complex, probably due to steric hindrance.



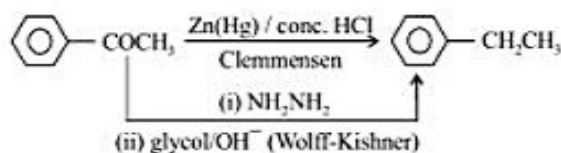
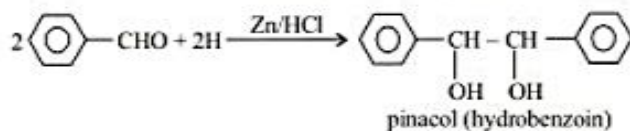
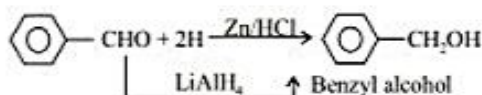
Benzaldehyde can react with hydrazine to form benzylideneazine.



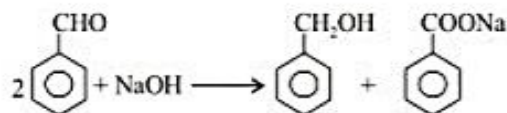
- Oxidation**



- Reduction**



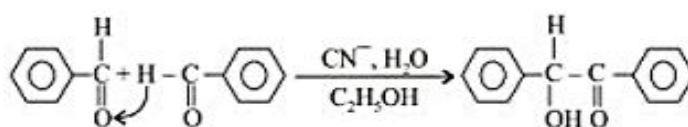
- Cannizzaro Reaction**



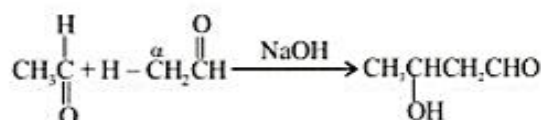
- It is given by those aldehydes which do not have H at  $\alpha$ -carbon, and also by HCHO.
- It is a disproportionation reaction.
- Benzoin condensation

When benzaldehyde is heated with aqueous ethanolic NaCN or KCN, it dimerises to form an  $\alpha$ -hydroxy ketone called benzoin, and reaction is called benzoin condensation.

It involves self condensation of an aromatic aldehyde in the presence of CN<sup>-</sup> as catalyst.

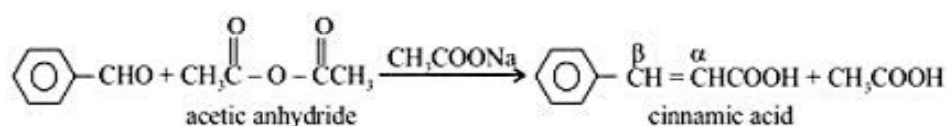


It resembles Aldol condensation of aliphatic aldehyde in which  $\alpha$ -H condenses, but -CHO group is free.



## PERKIN REACTION

It is the condensation reaction in which aromatic aldehyde is heated with an anhydride of an aliphatic acid in the presence of sodium salt of the same acid form  $\alpha$ ,  $\beta$ -unsaturated acid.

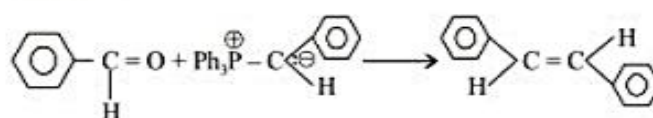
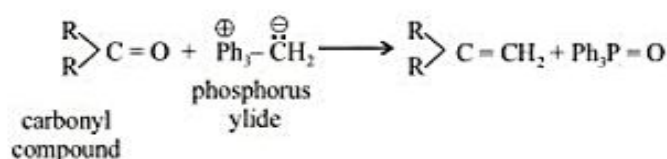


However, with cyclic anhydride (succinic anhydride),  $\beta$ ,  $\gamma$ -unsaturated acid is formed.

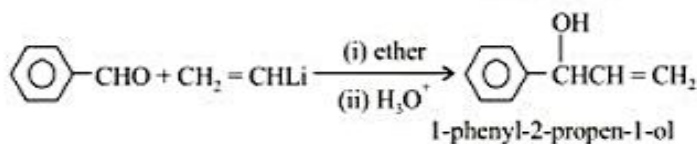
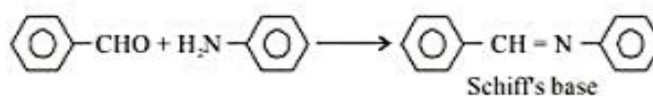


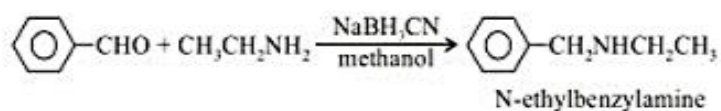
## Witting Reaction

It converts the carbonyl group of a ketone or aldehyde into a new double bond on reaction with phosphorus ylides.

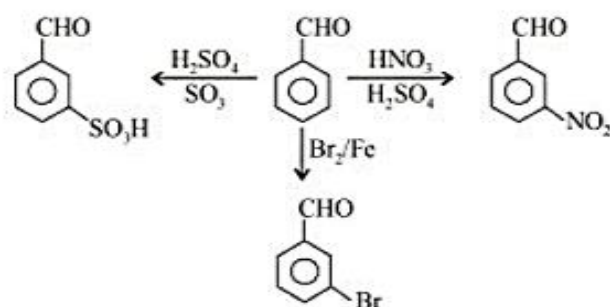
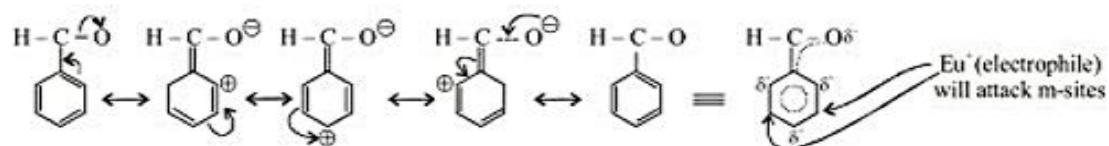


Mixture of cis and trans-isomers often result when geometric isomerism is possible.





• **Reactions of Benzene Nucleus**





## BIOMOLECULES (CARBOHYDRATES)

Carbohydrates (hydrates of carbon) are naturally occurring compounds having general formula  $C_x(H_2O)_y$ , which are constantly produced in nature & participate in many important bio-chemical reactions.

Ex.	Glucose	$C_6H_{12}O_6$	$C_6(H_2O)_6$
	Fructose	$C_6H_{12}O_6$	$C_6(H_2O)_6$
	Cellulose and Starch	$(C_6H_{10}O_5)_n$	

Sucrose (Cane sugar) -  $C_{12}H_{22}O_{11}$ , and Maltose (Malt Sugar)  $C_{12}(H_2O)_{11}$

But some compounds which have formula according to  $C_x(H_2O)_y$  are not known as carbohydrate

Ex.	$CH_2O$	Formaldehyde
	$C_2(H_2O)_2$	Acetic acid
	$C_3(H_2O)_3$	Lactic acid

There are many compounds, which show chemical behaviour of carbohydrate but do not confirm the general formula  $C_x(H_2O)_y$  such as -  $C_5H_{10}O_4$  (2-deoxyribose),  $C_6H_{12}O_5$  (Rahmnose)  
 $C_7H_{14}O_6$  (Rahmnohexose)

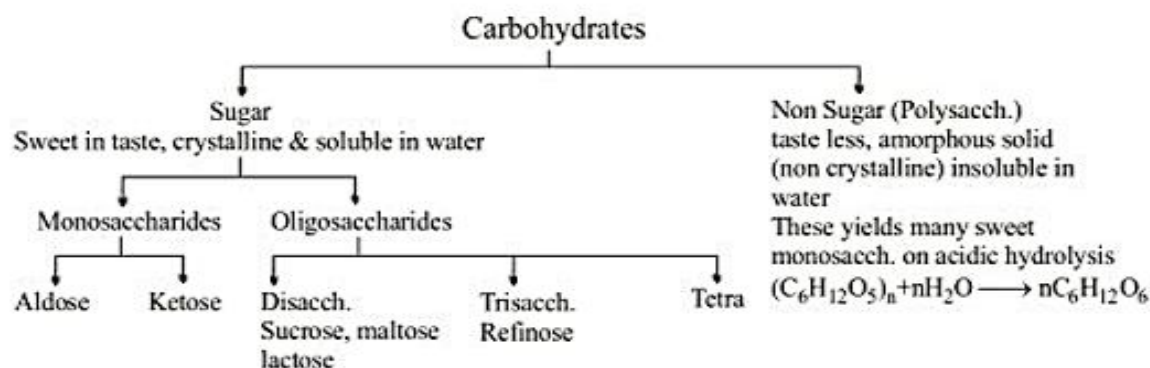
**Modern definition of carbohydrate:** Carbohydrates are polyhydroxy aldehyde or ketone  
 or

Substances which yield these (polyhydroxy aldehyde or ketone) on hydrolysis

Carbohydrates  $\xrightarrow{H^+/H_2O}$  Poly hydroxy aldehyde or ketone

Carbohydrates are also known as Saccharides.

### CLASSIFICATION OF CARBOHYDRATES



**Monosaccharides :** (simple sugars)

These are the sugars which cannot be hydrolysed into smaller molecules. General formula is  $C_nH_{2n}O_n$ .  
 Ex. - Glucose, Fructose, Ribose

**Oligosaccharides :**

These are the sugars which yields 2–10 monosaccharides units on hydrolysis. Such as.

**(a) Disaccharides :** Two monosaccharide unit on hydrolysis (may or may not be same).  
 Ex. - Sucrose, Maltose

**(b) Trisaccharides :** Three monosaccharide unit on hydrolysis.

**Polysaccharides :** These are the non sugars which yield a large no of monosaccharide units on hydrolysis General formula -  $(C_6H_{10}O_5)_n$  Ex.- Starch, Cellulose.

**Note :-** A group of polysaccharides which are not so widely used in nature is pentosans  $(C_5H_8O_4)_n$ . Monosaccharides, General formula  $C_x(H_2O)_y$ ,  $x = 3 - 8$ . Nomenclature of monosaccharides are given according to the no. of carbons present in them.

If  $-CHO$  group is present in monosaccharide, then it is known as aldose.

If  $-\overset{\overset{O}{\parallel}}{C}-$  group is present in monosaccharide, then it is known as ketose.

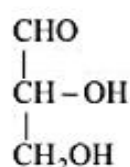
		<b>Aldoses</b>	<b>Ketoses</b>
3C	Triose or Triose	Aldotriose	Ketotriose
4C	Tetrose	Aldotetrose	Ketotetrose
5C	Pentose	Aldopentose	Ketopentose
5C	including $-CHO$	Aldopentose (Ribose)	$\begin{array}{c} H-C=O \\   \\ H-C-OH \\   \\ H-C-OH \\   \\ H-C-OH \\   \\ CH_2OH \end{array}$
5C	including $-\overset{\overset{O}{\parallel}}{C}-$	Ketopentose	$\begin{array}{c} CH_2OH \\   \\ C=O \\   \\ H-C-OH \\   \\ H-C-OH \\   \\ CH_2OH \end{array} \text{ (Ributose)}$
6C	Hexose	Aldohexose	Ketohexose
6C	including $-CHO$	Aldohexose (Glucose)	$\begin{array}{c} CHO \\   \\ H-C-OH \\   \\ HO-C-H \\   \\ H-C-OH \\   \\ H-C-OH \\   \\ CH_2OH \end{array}$ <p>D-glucose</p>
6C	including $-\overset{\overset{O}{\parallel}}{C}-$	Ketohexose (Fructose)	$\begin{array}{c} CH_2OH \\   \\ C=O \\   \\ HO-C-H \\   \\ H-C-OH \\   \\ H-C-OH \\   \\ CH_2OH \end{array}$ <p>D-fructose</p>

## STEREOCHEMISTRY OF CARBOHYDRATES :

**D & L-Sugars :** The series of aldoses or ketoses in which the configuration of the penultimate C-atom (C-next to  $\text{CH}_2\text{-OH}$  group) is described as D-sugars if  $\text{-OH}$  is towards RHS & L-sugars if it is towards LHS.

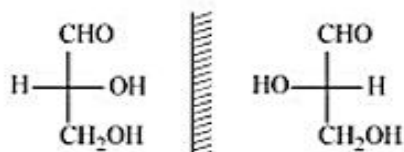
Smallest carbohydrate

Aldotriose



Glyceraldehyde

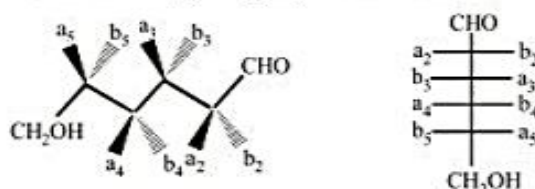
Fischer projection



D-Glyceraldehyde (+)

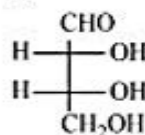
L-Glyceraldehyde (-)

Fischer formula of compounds containing many asymmetric carbon.

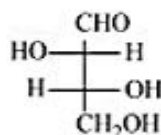


**Classification of Aldotetros :** (i) Erythrose  
(ii) Threose

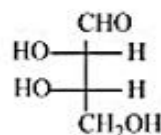
C-4



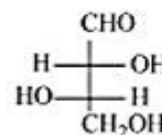
D-Erythrose



D-Threose

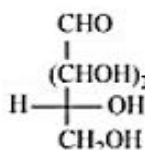


L-Erythrose

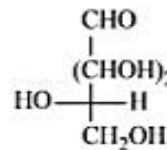


L-Threose

C-5



D-Aldopentose



L-Aldopentose

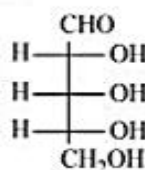
No. of  $\text{C}^* = 3$  (in Aldopentose)

No. of optical isomers  $2^3 = 8$

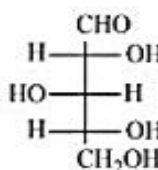
No. of D Sugars 4

No. of L Sugars 4

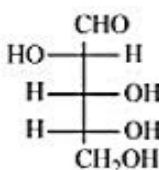
**D-Aldopentose :**



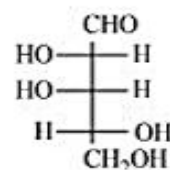
(I)



(II)



(III)



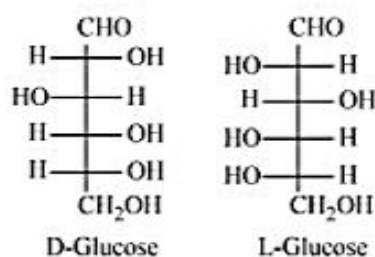
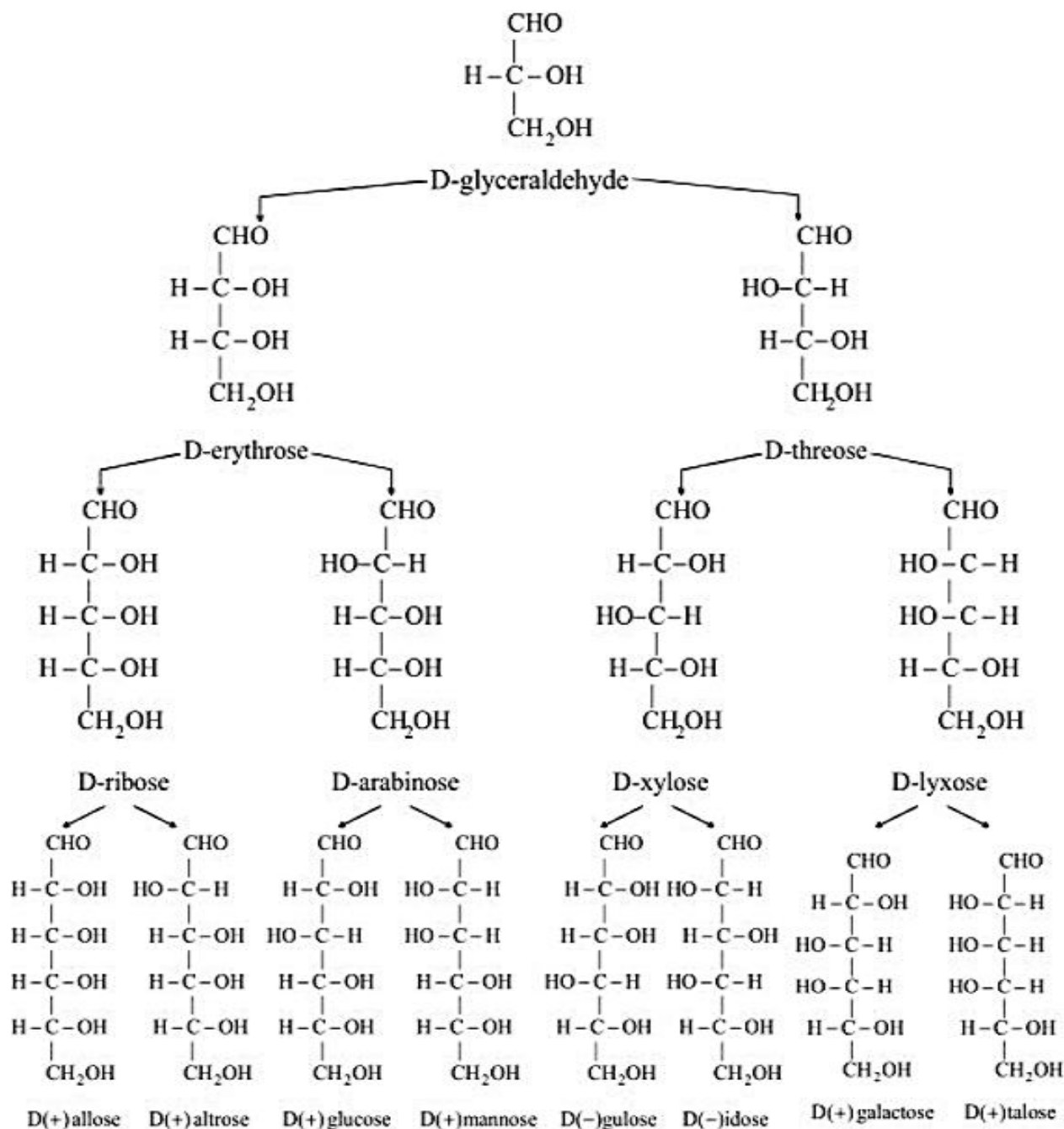
(IV)

All Isomeric D-sugars are diastereomers.

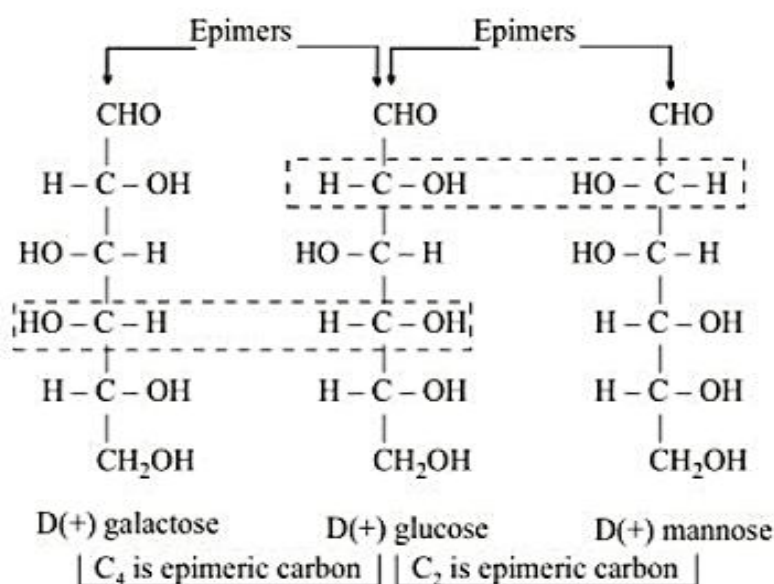
**Aldohexose :**No. of  $C^* = 4$ No. of stereoisomers =  $2^4 = 16$ 

No. of D-sugars = 8

No. of L-sugars = 8

**The D-family aldoses**






Another example with C<sub>2</sub> epimeric carbon is

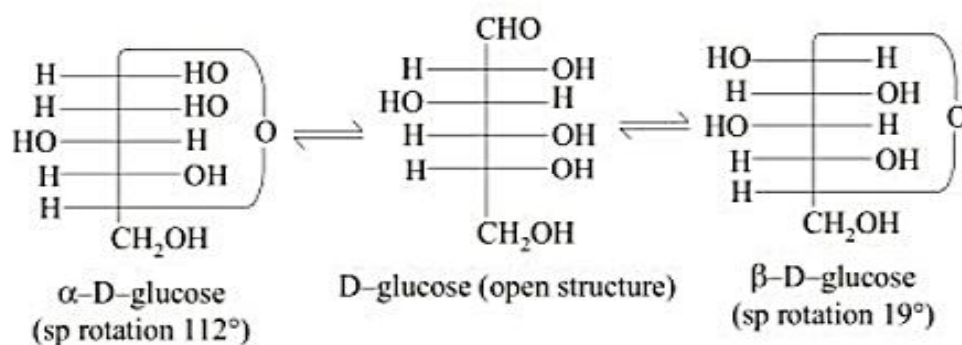


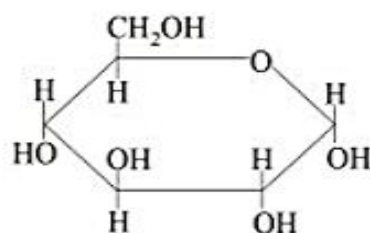
**Anomers:** Anomers are the stereoisomers which differ at a single chiral centre out of many & are ring chain tautomer of the same open chain compound.

The two sugars that differ in configuration only on the carbon that was the carbonyl carbon in the open chain form are called as anomers.  $\alpha$ -glucose and  $\beta$ -glucose are known as anomers. Their equilibrium mixture contains 36%  $\alpha$ -D-glucose, 63.8%  $\beta$ -D-glucose and 0.2% open chain form.

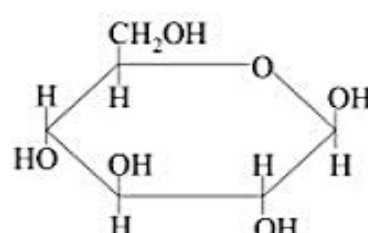
C<sub>1</sub> Carbon is known as anomeric carbon.

Haworth suggested to write  $\alpha$ -glucose and  $\beta$ -glucose in pyran structure 





Haworth formula  
 $\alpha$ -D-glucopyranose



Haworth formula  
 $\beta$ -D-glucopyranose

Anomers are epimers but epimers may not be anomers.

## CYCLIC STRUCTURES OF MONOSACCHARIDES

Many five membered and six membered monosaccharides occur in cyclic form. Cyclic structures of monosaccharides are established by many experiments. The cyclic structure is due to intramolecular hemiacetal formation between aldo / keto group and OH of any one carbon. The ring formed are generally six membered (pyranose) or five membered (furanose). Each cyclization results in creation of a new asymmetric centre apart from the existing ones. The isomers resulting from cyclizations are called anomers. Example, when D-glucose (open structure) cyclise, it gives  $\alpha$ -D-glucose and  $\beta$ -D-glucose.

### Haworth projection :

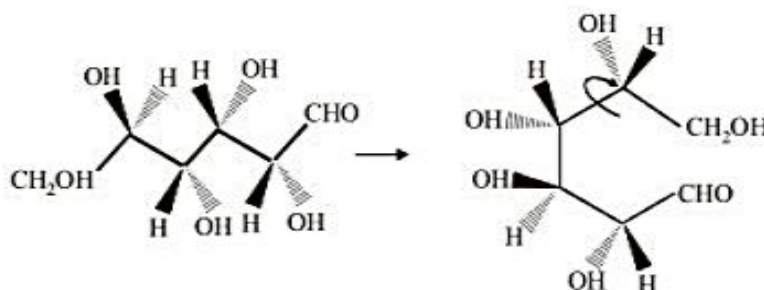
Many of monosaccharides form cyclic structures. The actual structure is almost planer and be represented by Haworth projection, which is a way of depicting three - dimensional cyclic structure.

**Rule -1 :** In a Haworth projection draw a fisher projection in which ring oxygen is in a down position.

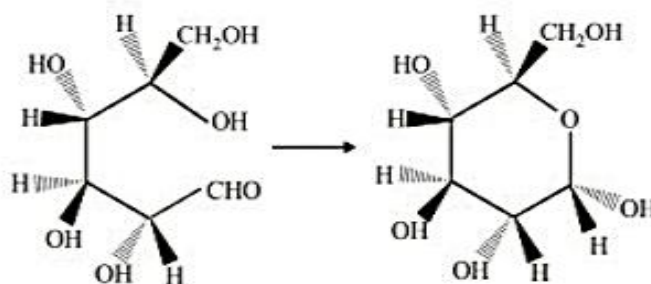
**Rule -2 :** Imagine that carbon chain of fisher projection is folded around a barrel or drum, which provide a ring lies in a plane  $\perp$  to the page.

**Rule -3 :** Now plane of ring is turned  $90^\circ$  so that anomeric carbon is on the right and the ring oxygen is in the rear. Obtained projection is a Haworth projection.

**Example :** (D-glucose)

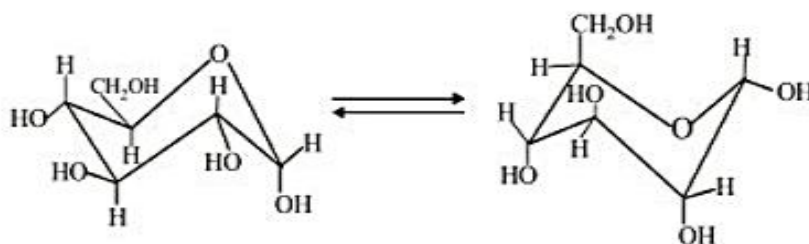


### Projection :

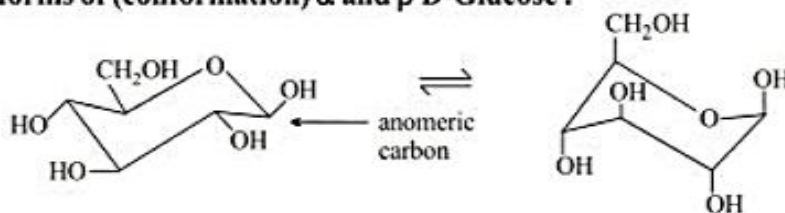


Hawarth projection

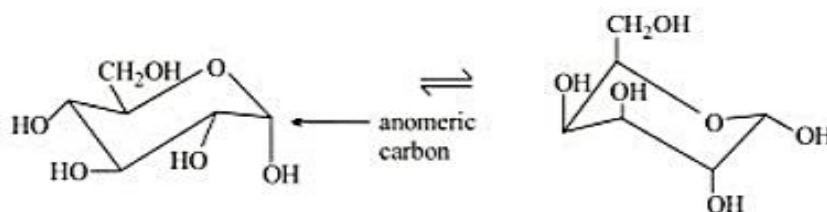
⇒ Chair conformation of D-glucose



**Chair forms of (conformation)  $\alpha$  and  $\beta$  D-Glucose :**

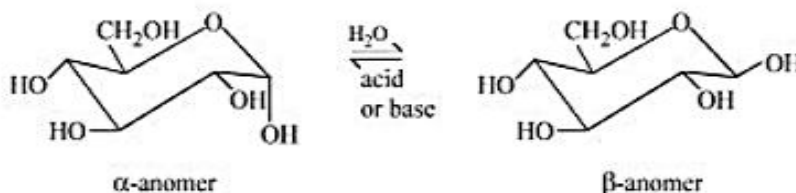


$\beta$ -D-Glucose (most stable glucose form) all groups are equatorial.



$\alpha$ -D-Glucose -OH group at anomeric carbon is axial.

**Mutarotation**



Specific rotation of  $\alpha$  glucose  $+112^\circ$

Specific rotation of  $\beta$  glucose  $+19^\circ$

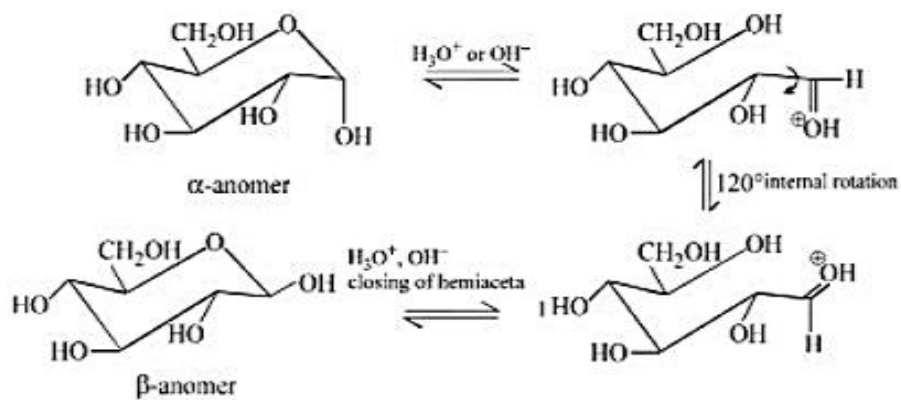
Equilibrium mixture  $[\alpha]_D = 52.5$  degree  $\text{mL g}^{-1} \text{dm}^{-1}$

Fresh $\alpha$ -glucose	→	52.5	←	Fresh $\beta$ -glucose
112°				19°
		36 % $\alpha$ glucose		
		63.8 % $\beta$ glucose		

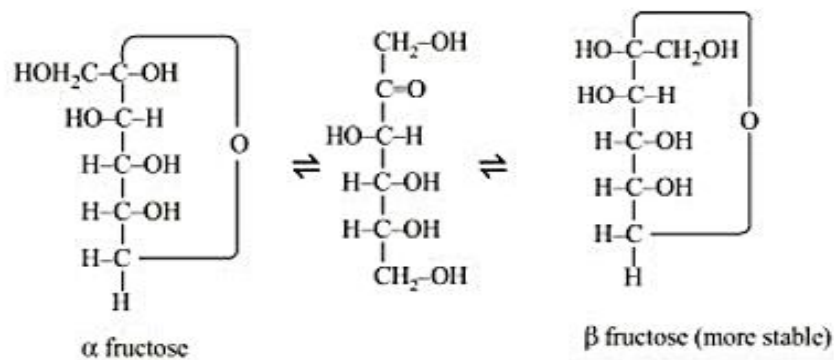
When pure  $\alpha$ -D glucose is dissolved in water its specific rotation is found to be  $+112^\circ$  with time, however the specific rotation of the solution decreases ultimately reaches stable value of  $+52.5^\circ$ . When  $\beta$  D-glucose is dissolved in water, it has a specific rotation of  $19^\circ$ . The specific rotation of this solution increases with time also to  $+52.5^\circ$ .

This change of optical rotation with time is called mutarotation. It is caused by the conversion of  $\alpha$  and  $\beta$  glucopyranose anomers into an equilibrium mixture of both. Mutarotation is catalyzed by both acid and base, but also occurs is even in pure water. Mutarotation is characteristic of the cyclic hemiacetal form of glucose.

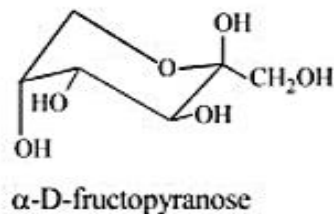
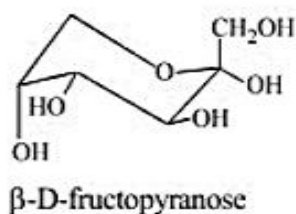
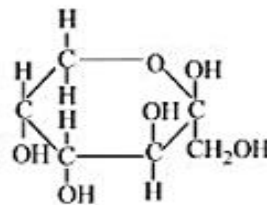
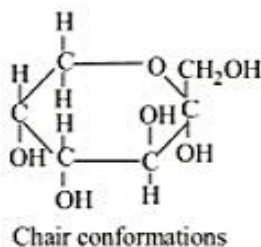
Mutarotation occurs first by opening of the pyranose ring to the free aldehyde form.



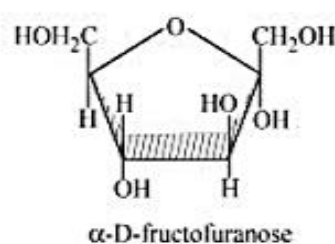
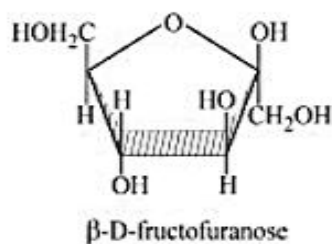
### Structure of fructose



Ring structure of fructose C, Pyranose structures 6 membered ring, C<sub>2</sub> – C<sub>6</sub> linkage

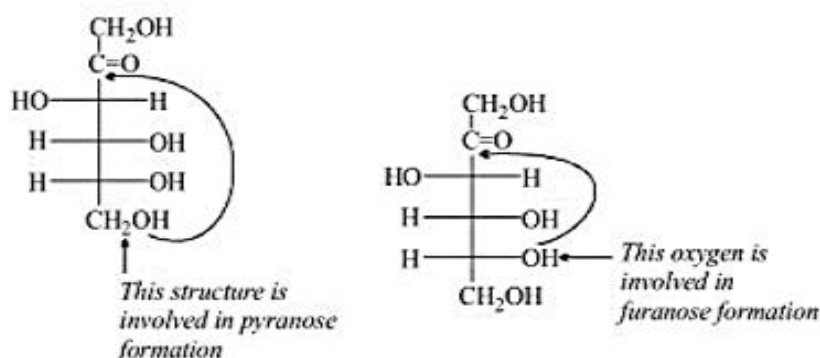


Furanose structure (5 membered ring)

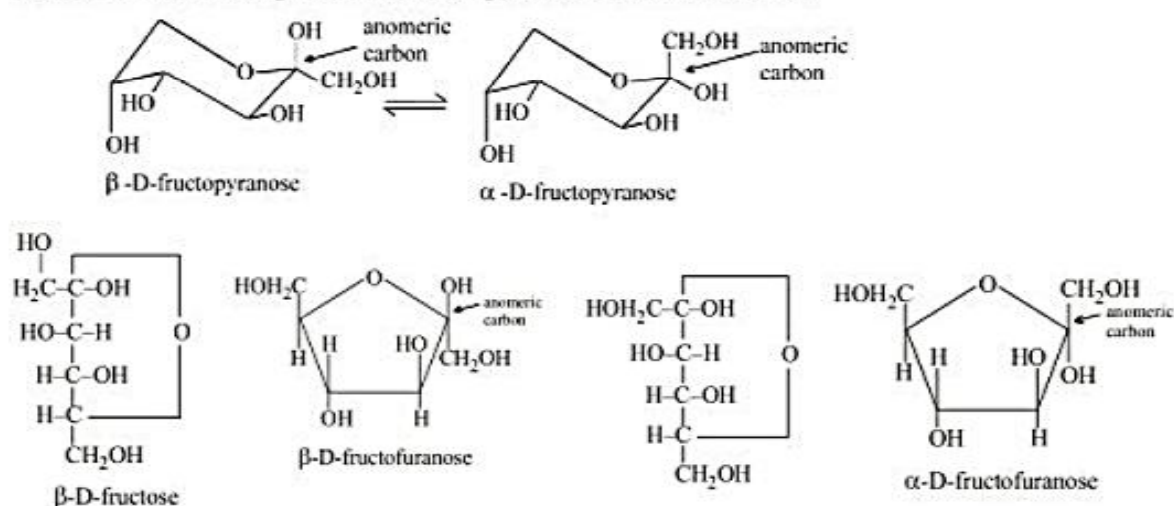




**Mutarotation:** Fructose undergo complex mutarotation. The structure of the cyclic hemiacetal form of d-fructose can be derived from it's carbonyl (Ketone) form using the methods described as follows.



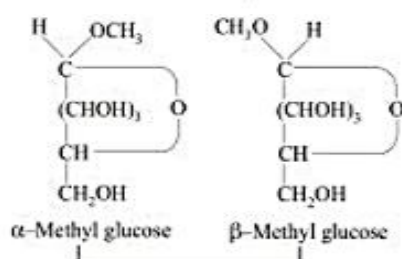
It happens that the crystalline form of D-fructose is  $\beta$ -D-Fructopyranose. When crystals of this form are dissolved in water, it equilibrates to both pyranose & furanose forms.



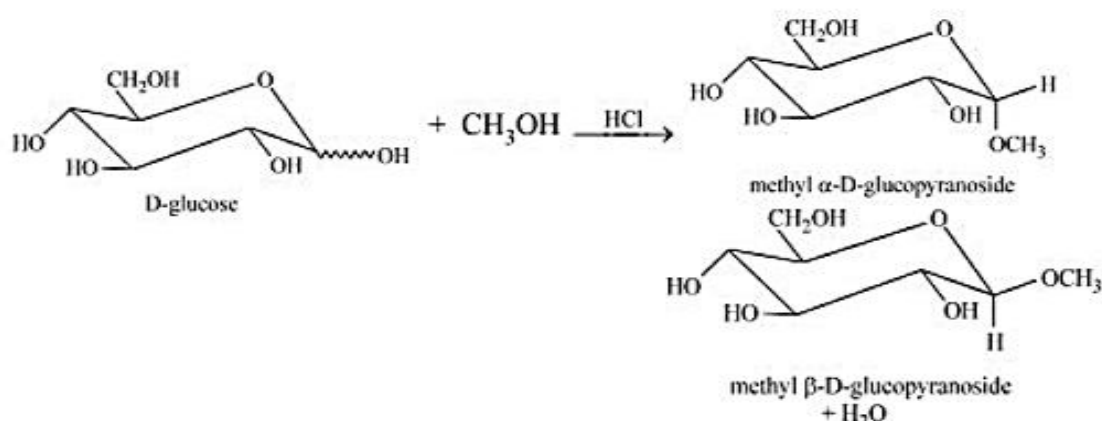
- \* All monosaccharides are reducing sugars, hence they show mutarotation.
- \* Starch, cellulose are Polymers of Glucose
- \* Lactose and sucrose are disaccharides
- \* Sucrose is a non reducing sugar, gives negative test for Benedict and tollen's reagent, they do not form osazone and do not show mutarotation.
- \* Acetals of carbohydrates are called as GLYCOSIDE

## FORMATION OF GLYCOSIDES

Glucose reacts with methyl alcohol in presence of dry HCl to form  $\alpha$  and  $\beta$ -methyl glycoside of glucose. The reaction takes place only on OH of hemi-acetylic carbon. Other hydroxyl groups are unreactive.



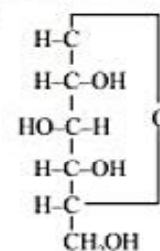
To methylate all the OH groups, methylating agent used is dimethyl sulphate.



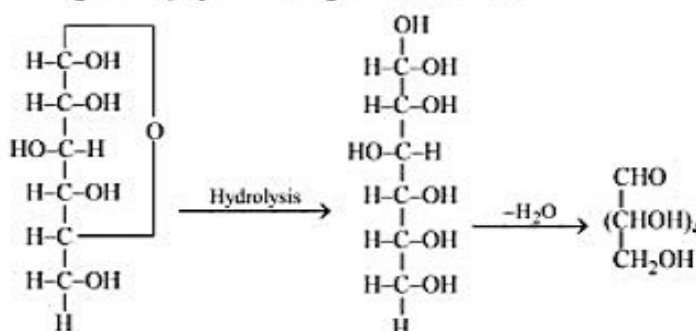
Such compounds are called glucoside (cyclic acetals). They are special type of acetals in which one of the oxygen of the acetal linkage is the ring oxygen of the pyranose or furanose.

### Ring structure of glucose :

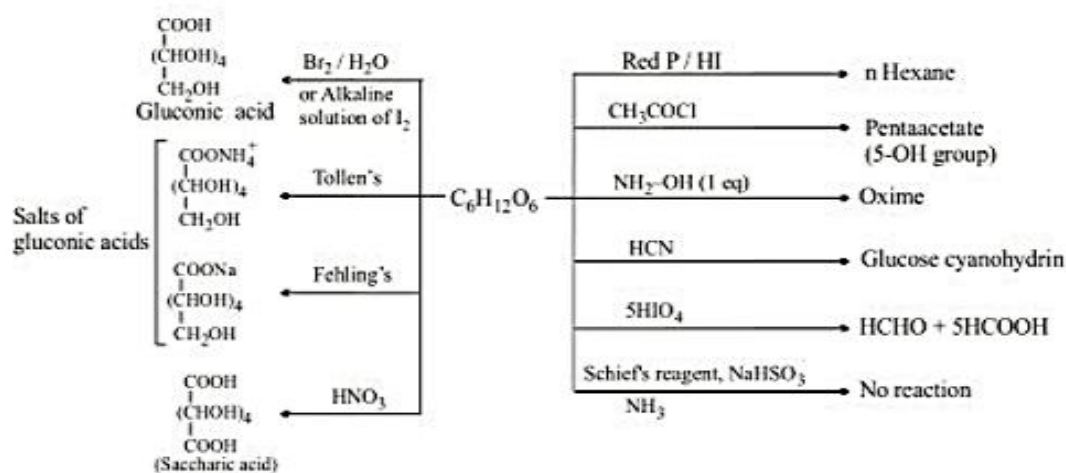
- (i) Glucose does not give pink colour with schief reagent.
- (ii) Does not form adduct with NaHSO<sub>3</sub>, NH<sub>3</sub>
- (iii) Glucose exist in two isomeric form
- (iv) It show mutarotation



Since there is no free aldehyde group, so it does not react with weak reagent (NH<sub>3</sub>, NaHSO<sub>3</sub>) but strong reagent (HCN, NH<sub>2</sub>OH, C<sub>6</sub>H<sub>5</sub>NH-NH<sub>2</sub>) break up ring

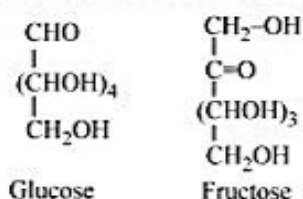


## REACTIONS OF GLUCOSE

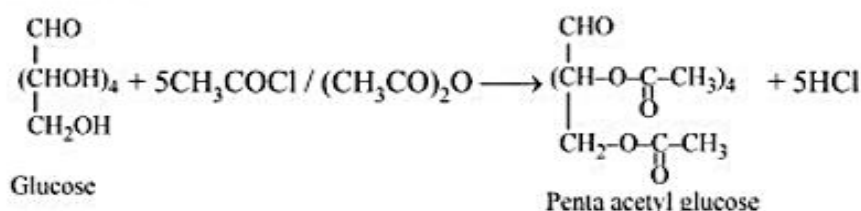


These reactions indicate that glucose has 6-C straight chain with one -CHO group & 5-OH group.

## GENERAL REACTIONS OF MONOSACCHARIDES

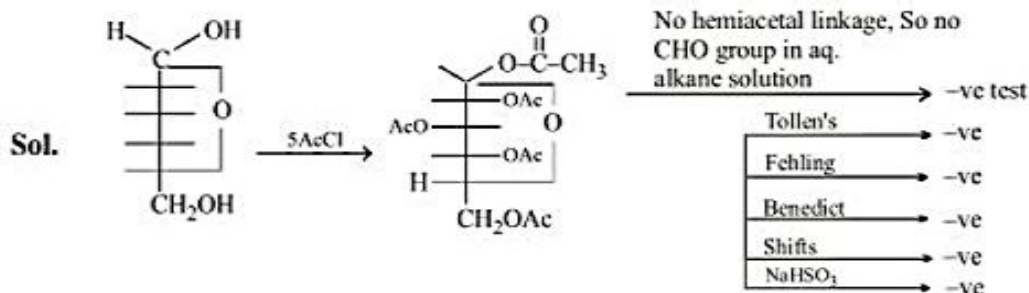


### 1. Acetylation :



This reaction suggests presence of 5(-OH) group.

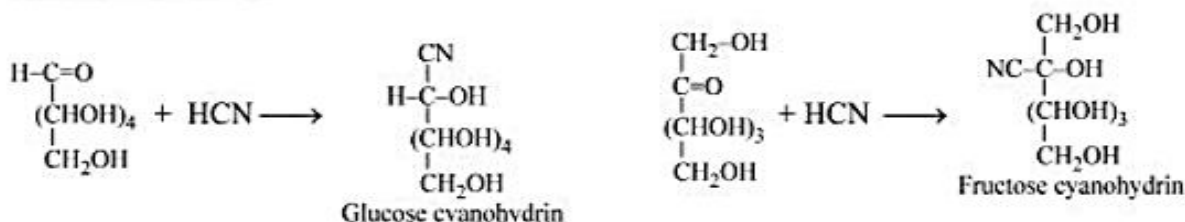
Q. The penta acetate of glucose give -ve test with Tollen's reagent & Fehling solution, explain?



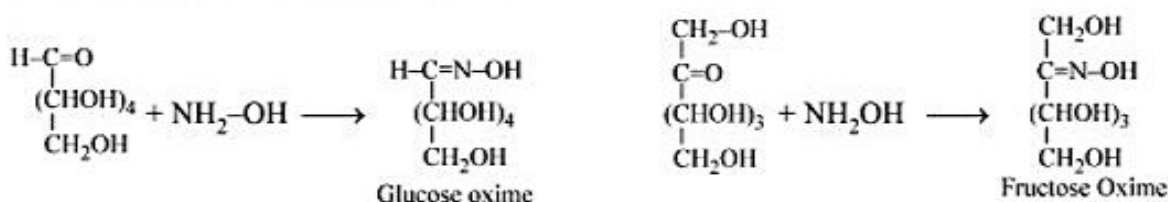
### 2. Red by HI / Red P:



### 3. Reaction with HCN:



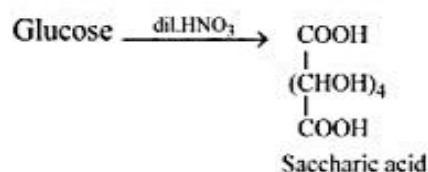
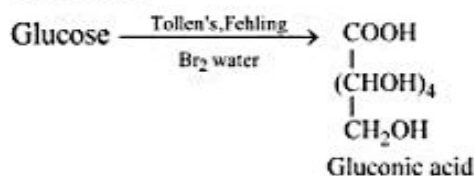
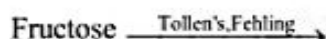
### 4. Reaction with NH<sub>2</sub>-OH (hydroxyl amine):



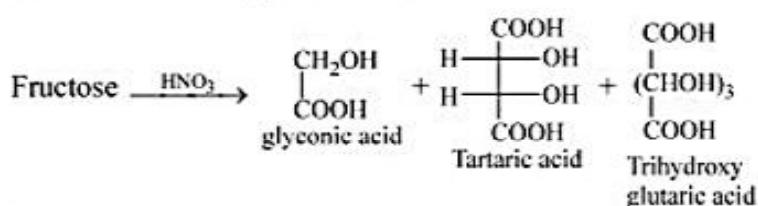
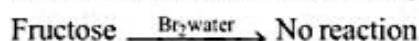




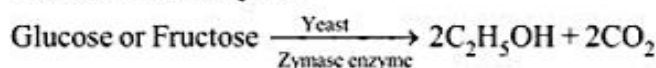
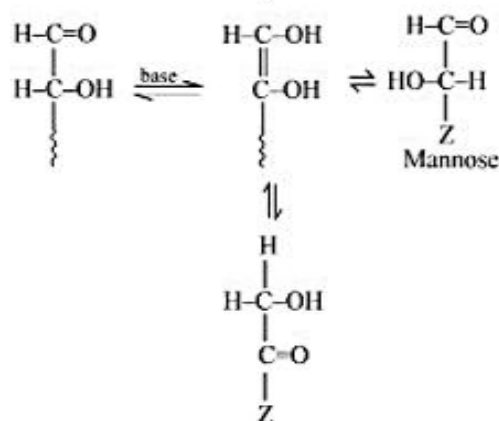
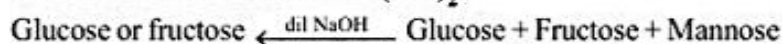
## 7. Oxidation:

**Oxidation of fructose :**

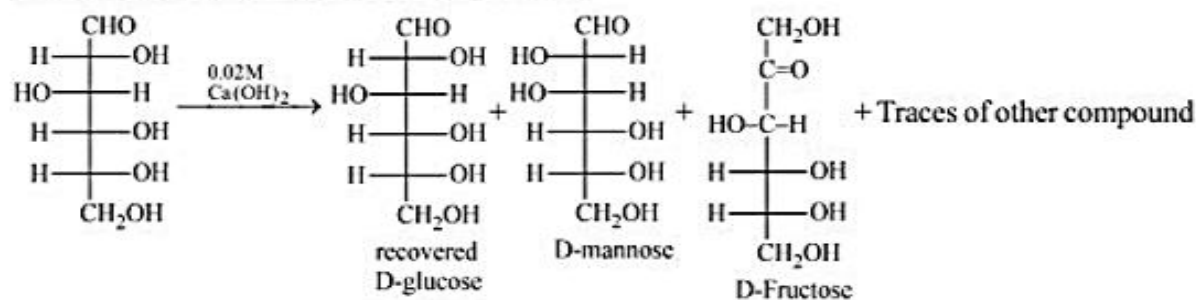
Fructose reduces tollen's & fehling reagent because in basic medium fructose isomerises to glucose.



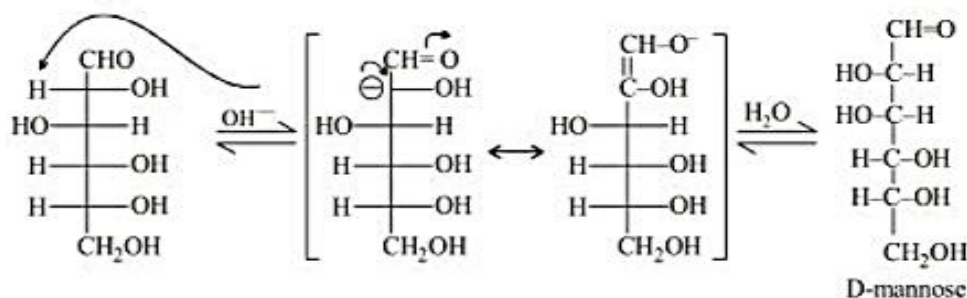
## 8. Reaction with enzyme:

9. Reaction with dil NaOH / Ca(OH)<sub>2</sub>**Base-catalyzed isomerisation of aldoses and Ketoses:**

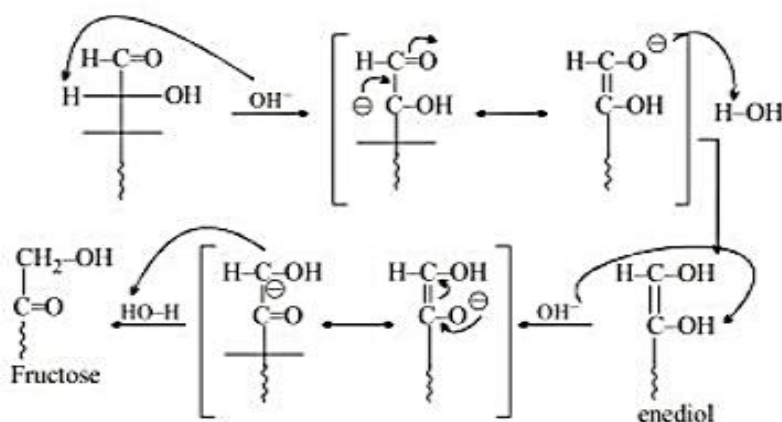
Although glucose in solution exists mostly in its cyclic hemiacetal forms it is also in equilibrium with a small amount of it's acyclic aldehyde form.



**Mechanism :** Like other aldehyde with  $\alpha$ -hydrogen, glucose ionise to give small amount of its enolate ion in base. Protonation of this enolate ion at one face of the double bond gives back glucose & protonation at the other face gives mannose.



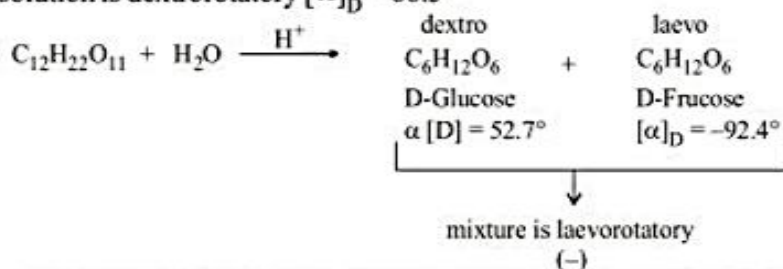
The enolate ion can also be protonated on oxygen to give a new enol called enediol this enediol converts to fructose as follows.



**Method of ascending the sugar series :** An aldose may be converted into its next higher aldose eg. an aldopentose into an aldohexose.

### SOME IMPORTANT CARBOHYDRATES

- Sucrose ( $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ) :**  $\rightarrow$  It is white, crystalline & sweet substance soluble in water obtained from the sugar cane. When heated above its melting point, it forms a brown substance known as caramel. Its aqueous solution is dextrorotatory  $[\alpha]_D = 66.5^\circ$

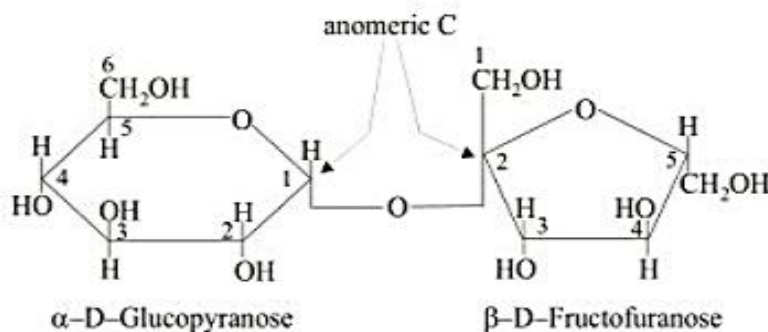


Thus hydrolysis of sucrose brings about a change in the sign of rotation, from dextro (+) to leavo (-) & such a change is known as inversion of cane sugar and the mixture is known as *invert sugar*.

The inversion of cane-sugar may also be effected by the enzyme invertase which is found in yeast.

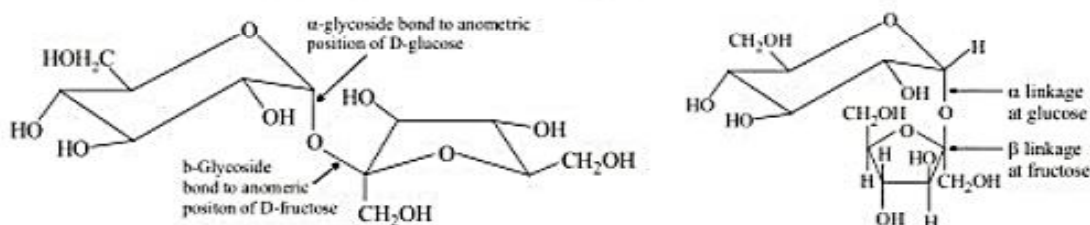
Sucrose is non-reducing sugar because it has stable acetal linkage & in aq. solution it can not give free carbonyl group and so it does not reduce Tollen's & Fehling's solution.

This indicates that neither the aldehyde group of glucose nor the ketonic group of fructose is free in sucrose.

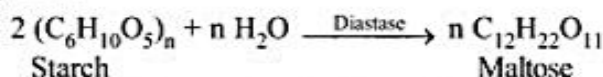


All non reducing sugars do not show mutarotation .

There is no free carbonyl group so it is non reducing sugar



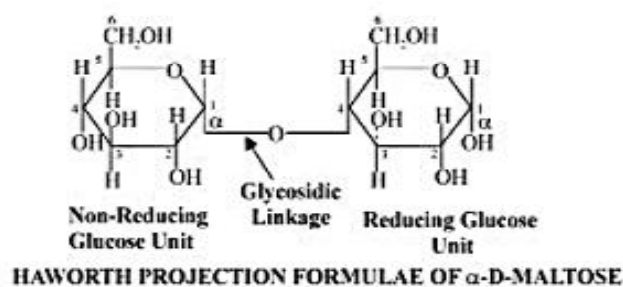
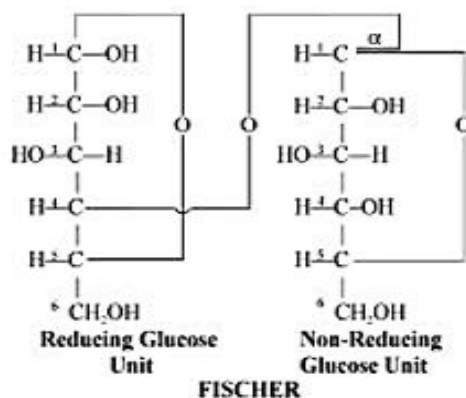
2. **Maltose:** It is obtained by partial hydrolysis of starch by the enzyme diastase present in malt i.e., sprouted barely seeds.



As stated above, hydrolysis of one mole of maltose yields two moles of D-glucose. Maltose is a reducing sugar since it forms an osazone, undergoes mutarotation and also reduces Tollen's and Fehling's solutions, Methylation studies have revealed that

- (i) both glucose units are present in the pyranose form.
- (ii)  $\text{C}_1$  of one glucose unit is linked to  $\text{C}_4$  of the other

Further since maltose is hydrolysed by the enzyme maltase which specifically hydrolyses  $\alpha$ -glycosidic linkage, therefore, the non-reducing glucose unit in maltose must be present in the  $\alpha$ -form. In other words,  $\text{C}_1 - \alpha$  of non-reducing glucose unit is attached to  $\text{C}_4$  of the reducing glucose unit as shown in the figure on next page.





### 3. Lactose (Milk sugar) $C_{12}H_{22}O_{11}$

Lactose occurs in milk and that is why it is called milk sugar.

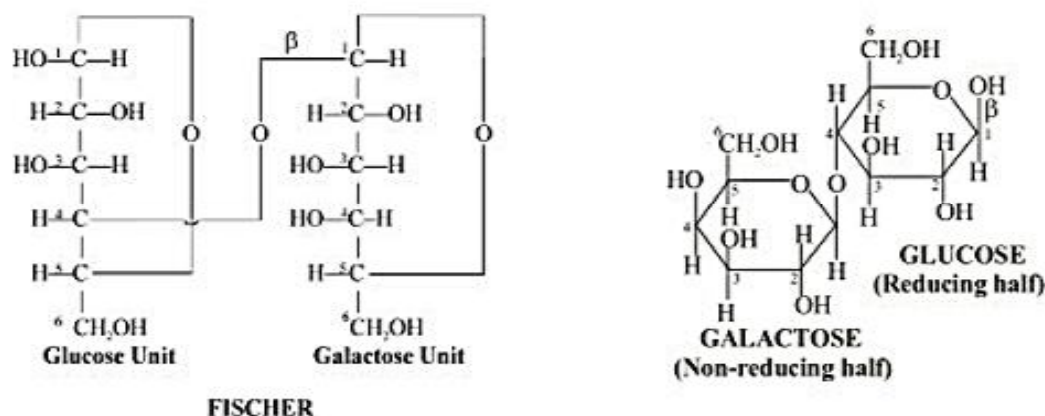
Lactose on hydrolysis with dilute acid or by enzyme lactase, yields an equimolar mixture of D-glucose and D-galactose. It is a reducing sugar since it forms an osazone, undergoes mutarotation and also reduces Tollen's or Fehling's solution. Methylation studies have revealed that

(i) both glucose and galactose are present in the pyranose form.

(ii) glucose is the reducing half while  $\beta$ -galactose is the non-reducing half.

(iii)  $C_1$  of galactose unit is connected to  $C_4$  of glucose unit.

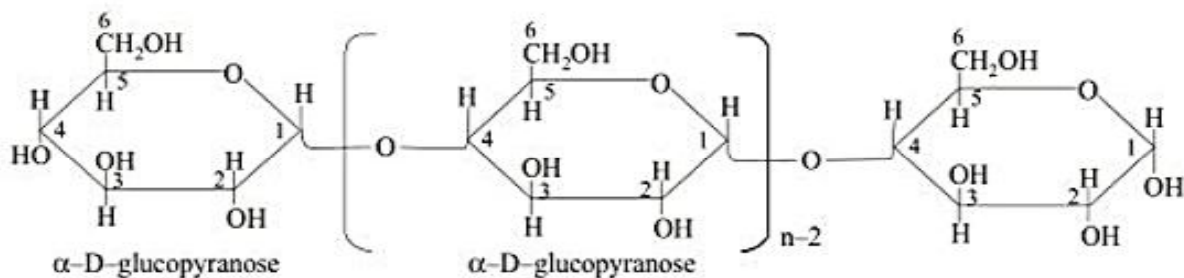
Further since emulsin, as, enzyme which specifically hydrolyses  $\beta$ -glycosidic linkages also hydrolyses lactose, therefore, galactose must be present in the  $\beta$ -form. In other words, in lactose,  $C_1 - \beta$  of galactose is attached to  $C_4$  of glucose as shown in figure.



### 4. Starch Amylum, $(C_6H_{10}O_5)_n$

**Occurrence :** The value of  $n$  (100 – 3000) varies from source to source. It is the chief food reserve material or storage polysaccharide of plants and is found mainly in seeds, roots tubers etc. Wheat, maize, rice, potatoes, barley, bananas and sorghum are the main sources of starch. Starch occurs in the form of granules, which vary in shape and size depending upon their plant source.

Occurs in all green plants. Starch consists of two fractions, one being known as  $\alpha$ -amylose, which gives blue colour with iodine. This blue colour is believed to be due to the formation of an inclusion complex. An aqueous solution of  $\alpha$ -amylose slowly forms a precipitate, since  $\alpha$ -amylose has a strong tendency to 'revert' to the insoluble state in solution. Amylopectin is insoluble in water and is stable towards both hydrolysis to maltose by the enzyme diastase and to D(+)-glucose by dilute acids (amylopectin gives about 50 percent of maltose).



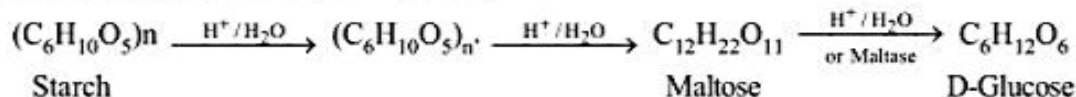
Structure of Starch ( $\alpha$ -D-glucosamylose)

$\alpha$ -amylose consists of an unbranched chain, with a molecular weight varying between 10,000 ( $n \approx 60$ ) and 10,00,000 ( $n \approx 6,000$ ). The value of  $n$  depends on the source and treatment of  $\alpha$ -amylose.



**Properties :** (i) Starch is a white amorphous powder sparingly soluble in water. Its aqueous solution gives a blue colour with iodine solution due to the formation of an inclusion complex. The blue pears on cooling.

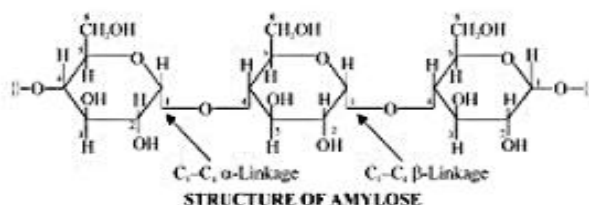
(ii) On hydrolysis with dilute mineral acids or enzymes, starch breaks down first to smaller molecules ( $n > n'$ ), then to maltose and finally to D-glucose.



(iii) Starch is a non-reducing saccharide. It neither reduces Tollen's reagent or Fehling's solution nor forms an osazone. This suggests that all hemiacetal OH groups of glucose units at  $C_1$  are not free but are involved in glycosidic linkages.

**Composition :** Starch is not a single compound but is a mixture of two components—a water soluble component called amylose (10-20%) and a water insoluble component called amylopectin (80-90%). Both amylose and amylopectin are polymers of  $\alpha$ -D-glucose.

**Structure of amylose :** Amylose is water soluble and gives blue colour with iodine solution. It may have 100-3000 glucose units, i.e., its molecular mass can vary from 10,000 to 500,000. It is a linear polymer of  $\alpha$ -D-glucose in which  $C_1$  of one glucose unit is attached to  $C_4$  of the other through  $\alpha$ -glycosidic linkage as shown in figure.



### Pectins

Pectins are found in plant and fruit juices. Their characteristic property is the ability of their solutions to gelate, i.e. form jellies. They have a high molecular weight and are polygalacturonic acid (linked 1,4) with the carboxyl groups partially esterified with methanol.

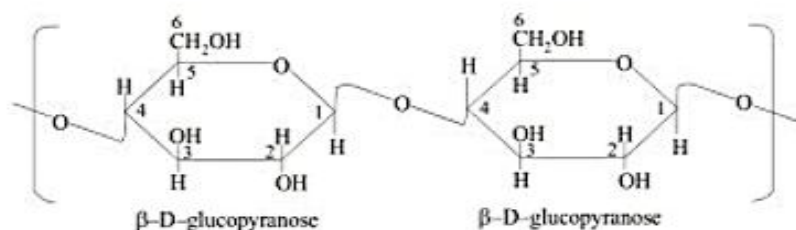
### Glycogen ( $C_6H_{10}O_5$ )<sub>n</sub> :

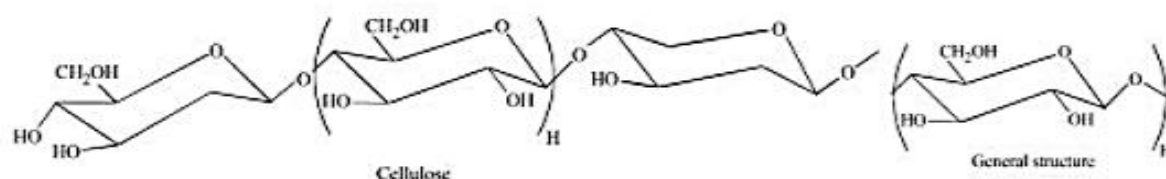
Glycogen is found in nearly all animals cells, occurring mainly in liver. It is the reserve carbohydrate of animals and so is often known as 'animal starch'. It has also been isolated from plant sources.

Glycogen is a white powder, soluble in water, the solution giving a purplish-red colour with iodine. On hydrolysis with dilute acid, glycogen gives D(+)-glucose. The molecular weight of glycogen has been given as 10,00,000 to 50,00,000 and glycogen contains highly branched chains. Glycogen has a structure similar to amylopectin, except that it has more cross-linking.

## 5. Cellulose:

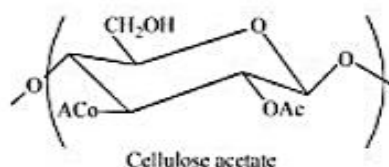
Cellulose is colourless, solid which is insoluble in water & organic solvents. But it is soluble in ammoniacal cupric hydroxide (Schweizer's reagent) or in conc. HCl cellulose is a regular polymer of d-glucopyranose residues connected by  $\beta$ -1,4 glycosidic linkages. It is straight chain polymer.





### Some points about cellulose :

1. General empirical formula ( $C_6H_{10}O_5$ )
2.  $\text{Cellulose} + H_2O \xrightarrow{H^+} 96\% \text{ of crystalline D-glucose}$
3. No. of monomer units in cellulose are 1000 – 1500 in one molecule.
4. Cellulose doesn't show mutarotation (like starch)
5. It is non reducing sugar because there is no hemiacetal linkage.
6. Acetylations nitration & methylation of cellulose give trisubstituted cellulose which suggest that only three –OH groups are free.



### Tests for carbohydrates:

- (i) When heated in a dry test tube, it melts, turns brown and finally black, giving a characteristic smell of burning sugar.
- (ii) When warmed with a little concentrated  $H_2SO_4$ , it leaves a charred residue of carbon.
- (iii) **Molisch's Test** (named after Austrian botanist Hans Molisch) is a sensitive chemical test for the presence of carbohydrates, based on the dehydration of the carbohydrate by sulfuric acid to produce an aldehyde, which condenses with two molecules of phenol (usually  $\alpha$ -naphthol, though other phenols (e.g. resorcinol, thymol) also give colored products) resulting in a red- or purple-colored compound.

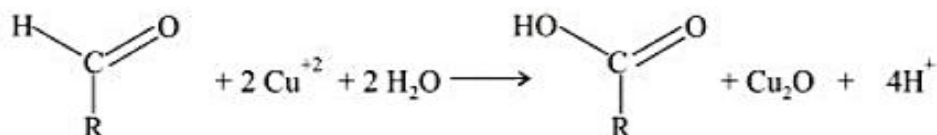
The test solution is combined with a small amount of Molisch's reagent ( $\alpha$ -naphthol dissolved in ethanol) in a test tube. After mixing, a small amount of concentrated sulfuric acid is slowly added down the sides of the sloping test-tube, without mixing, to form a bottom layer. A positive reaction is indicated by appearance of a purple ring at the interface between the acid and test layers.

All carbohydrates — monosaccharides, disaccharides, and polysaccharides — should give a positive reaction, and nucleic acids and glycoproteins also give a positive reaction, as all these compounds are eventually hydrolyzed to monosaccharides by strong mineral acids. Pentoses are then dehydrated to furfural, while hexoses are dehydrated to 5-hydroxymethylfurfural. Either of these aldehydes, if present, will condense with two molecules of naphthol to form a purple-colored product, as illustrated below by the example of glucose:



## BARFOED'S TEST

**Barfoed's Test** is a chemical test used for detecting the presence of monosaccharides. It is based on the reduction of copper (II) acetate to copper (I) oxide ( $\text{Cu}_2\text{O}$ ), which forms a brick-red precipitate. Barfoed's reagent consists of a 0.33 molar solution of neutral copper acetate in 1% acetic acid solution. The reagent does not keep well and it is therefore advisable to make it up when it is actually required. Reducing monosaccharides are oxidized by the copper ion in solution to form a carboxylic acid and a reddish precipitate of copper (I) oxide within three minutes. Reducing disaccharides undergo the same reaction, but do so at a slower rate and ppt. will come after 10 min. For Non reducing saccharides ppt. will not form.



The aldehyde group of the monosaccharide which normally forms a cyclic hemiacetal is oxidized to the carboxylate. A number of other substances, including sodium chloride may interfere.

## STARCH

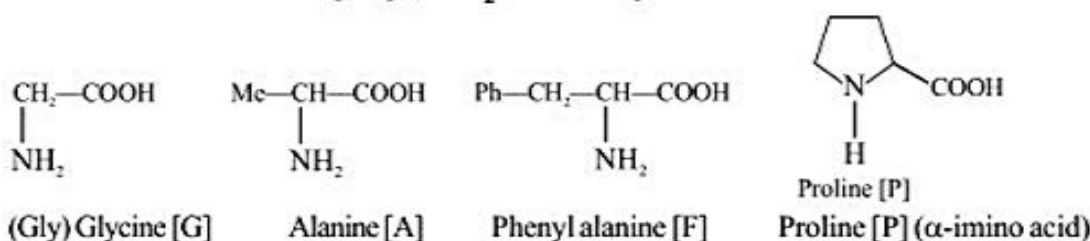
Plants store glucose as the polysaccharide starch. The cereal grains (wheat, rice, corn, oats, barley) as well as tubers such as potatoes are rich in starch.

Starch can be separated into two fractions--amylose and amylopectin. Natural starches are mixtures of amylose (10-20%) and amylopectin (80-90%).

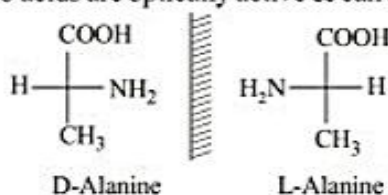
**Iodine - KI Reagent:** Iodine is not very soluble in water, therefore the iodine reagent is made by dissolving iodine in water in the presence of potassium iodide. This makes a linear triiodide ion complex with is soluble. The triiodide ion slips into the coil of the starch causing an intense blue-black color.

## AMINO ACIDS AND PROTEINS

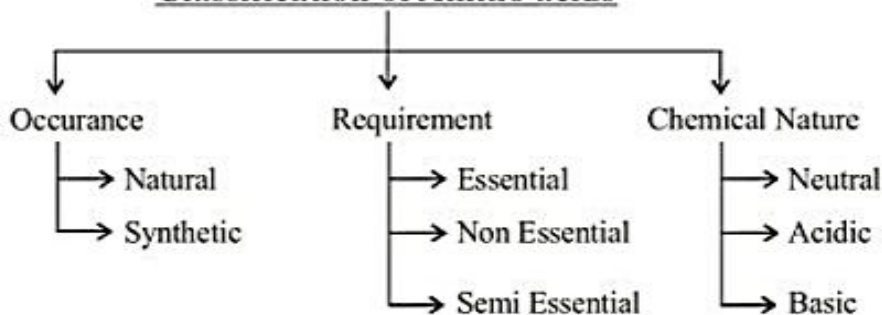
Bifunctional compounds  $\text{R}-\text{CH}(\text{NH}_2)-\text{COOH}$  having an acidic carboxylic group & a basic amino group. There are 20 amino acids commonly found in proteins and are standard amino acids. All are  $\alpha$  amino acids. Most of them have  $1^\circ$  amino group ( $-\text{NH}_2$ ). However proline is a  $2^\circ$  amino



All amino acids are chiral molecules with at least one chiral carbon except glycine,  $\text{H}_3\text{N}^+\text{CH}_2\text{COO}^-$ . Except Glycine all other amino acids are optically active & can be assigned D & L configuration.



### Classification of Amino acids



#### **Based on requirement**

1. Essential amino acids can not be synthesized in human body so dietary intake is required. For any human being 1 gm a day is required.
2. Semi essential amino acids can be synthesized in human body but dietary intake is required during growing stages (when more of cell division is required).  
For example : Early childhood, pregnancy and lactating mother.
3. Non essential amino acid - Body can synthesize them.

#### **Chemical classification**

**Neutral** - Amino acid having equal number of  $\text{NH}_2$  and  $\text{COOH}$ .

Neutral amino acids are further classified as polar and nonpolar depending on whether their side chains have polar substituents (for example, asparagine with an  $\text{NH}_2\text{CO}$  group) or are completely hydrocarbon in nature (for example alanine, valine etc.).

**Acidic** - Amino acid having more  $\text{COOH}$  than  $\text{NH}_2$

Aspartic acid and glutamic acids, each with a second  $\text{CO}_2\text{H}$  in their side chain are acidic amino acids.

**Basic** - Amino acid having more  $\text{NH}_2$  than  $\text{COOH}$

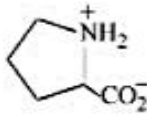
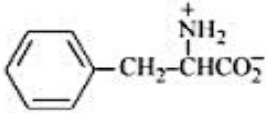
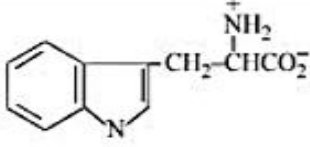
Lysine, arginine and histidine, each with a basic site in their side chain are basic amino acids.

**Proteins:** The name protein is taken from the Greek word "proteios", which means "first". Of all chemical compounds, proteins must almost certainly be ranked first, for they are the substance of life.

Proteins make up a large part of the animal body, they hold it together and they run it. They are found in all living cells.



Chemically, proteins are high polymers. They are polyamides and the monomers from which they are derived are the  $\alpha$  - amino carboxylic acids. A single protein molecule contains hundreds or even thousands of amino acid units. These units can be of twenty-odd different kinds. The number of different combinations, i.e., the number of different protein molecules that are possible, is almost infinite.

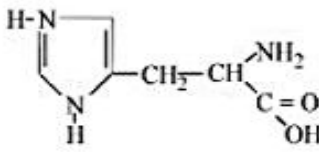
<i>I. Neutral amino acids (with nonpolar side chains)</i>			
NAME	ABBREVIATIONS	STRUCTURAL FORMULAE	ISOELECTRIC POINT[pI]
@Glycine	Gly(G)	$\begin{array}{c} \text{NH}_2 \\   \\ \text{H}_2\text{C} \\   \\ \text{C}=\text{O} \\   \\ \text{OH} \end{array}$	6.0
Alanine	Ala(A)	$\begin{array}{c} \text{NH}_2 \\   \\ \text{H}_3\text{C}-\text{CH} \\   \\ \text{C}=\text{O} \\   \\ \text{OH} \end{array}$	6.0
Valine*	Val(V)	$\begin{array}{c} \text{H}_3\text{C}-\text{CH}-\text{C}-\text{NH}_2 \\   \quad \quad   \\ \text{CH}_3 \quad \quad \text{C}=\text{O} \\ \quad \quad \quad   \\ \quad \quad \quad \text{OH} \end{array}$	6.0
Leucine*	Leu(L)	$\begin{array}{c} \text{H}_3\text{C}-\text{CH}-\text{CH}_2-\text{C}-\text{NH}_2 \\   \quad \quad \quad   \\ \text{CH}_3 \quad \quad \quad \text{C}=\text{O} \\ \quad \quad \quad   \\ \quad \quad \quad \text{OH} \end{array}$	6.0
Isoleucine*	Ile(I)	$\begin{array}{c} \text{CH}_3 \quad \text{NH}_3^+ \\   \quad   \\ \text{CH}_3\text{CH}_2\text{CH}-\text{CHCO}_2^- \end{array}$	6.0
Methionine*	Met(M)	$\begin{array}{c} \text{NH}_3^+ \\   \\ \text{CH}_3\text{SCH}_2\text{CH}-\text{CHCO}_2^- \end{array}$	5.7
@@Proline	Pro(P)		6.3
Phenylalanine*	Phe(F)		5.5
Tryptophan*	Trp(W)		5.9

**2. Neutral amino acids (with polar, but nonionized side chains)**

NAME	ABBREVIATIONS	STRUCTURAL FORMULAE	ISOELECTRIC POINT[pI]
Asparagine	Asn(N)	$\text{H}_2\text{N}-\overset{\text{O}}{\underset{\text{  }}{\text{C}}}-\text{CH}_2-\underset{\text{C}=\text{O}}{\overset{\text{NH}_2}{\text{CH}}}-\text{OH}$	5.4
Glutamine	Gln(Q)	$\text{H}_2\text{N}-\overset{\text{O}}{\underset{\text{  }}{\text{C}}}-\text{CH}_2-\text{CH}_2-\underset{\text{C}=\text{O}}{\overset{\text{NH}_2}{\text{CH}}}-\text{OH}$	5.7
Serine	Ser(S)	$\text{HO}-\text{CH}_2-\underset{\text{C}=\text{O}}{\overset{\text{NH}_2}{\text{CH}}}-\text{OH}$	5.7
Threonine*	Thr	$\begin{array}{c} \text{OH} \quad \text{NH}_3^+ \\   \quad   \\ \text{CH}_3\text{CH}-\text{CHCO}_2^- \end{array}$	5.6
Tyrosine	Tyr(Y)	$\text{HO}-\text{C}_6\text{H}_4-\text{CH}_2-\underset{\text{C}=\text{O}}{\overset{\text{NH}_2}{\text{CH}}}-\text{OH}$	5.7
Cysteine	Cys	$\text{HSCH}_2-\underset{\text{C}=\text{O}}{\overset{\text{NH}_3^+}{\text{CH}}}-\text{OH}$	5.1
± Cystine	Cys-Cys	$\begin{array}{c} \text{NH}_3^+ \quad \text{NH}_3^+ \\   \quad   \\ ^-\text{OOCCHCH}_2\text{S}-\text{SCH}_2\text{CHCOO}^- \end{array}$	

**3. Acidic amino acids (side chain with carboxylic acid group)**

NAME	ABBREVIATIONS	STRUCTURAL FORMULAE	ISOELECTRIC POINT[pI]
Aspartic acid	Asp(D)	$\text{HO}-\overset{\text{O}}{\underset{\text{  }}{\text{C}}}-\text{CH}_2-\underset{\text{C}=\text{O}}{\overset{\text{NH}_2}{\text{CH}}}-\text{OH}$	2.8
Glutamic Acid	Glu(E)	$\text{O}=\underset{\text{OH}}{\text{C}}-\text{CH}_2-\text{CH}_2-\underset{\text{C}=\text{O}}{\overset{\text{NH}_2}{\text{CH}}}-\text{OH}$	3.2

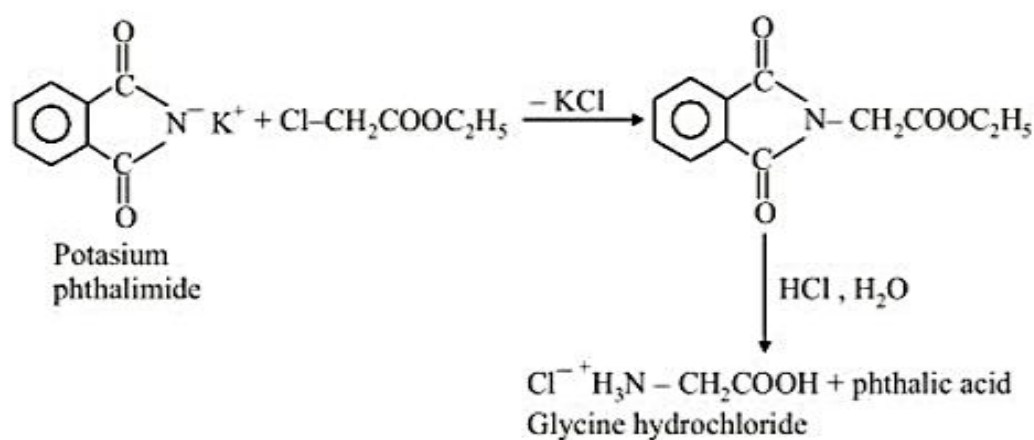
4. Basic amino acids (side chain with nitrogenous basic group)			
NAME	ABBREVIATIONS	STRUCTURAL FORMULAE	ISOELECTRIC POINT [pI]
Lystine*	Lys(K)	$\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH} \begin{array}{l} \nearrow \text{NH}_2 \\ \searrow \text{C}=\text{O} \\ \quad \text{OH} \end{array}$	9.7
Arginine*	Arg(R)	$\text{H}_2\text{N}-\overset{\text{NH}}{\underset{\text{  }}{\text{C}}}-\text{NH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH} \begin{array}{l} \nearrow \text{NH}_2 \\ \searrow \text{C}=\text{O} \\ \quad \text{OH} \end{array}$	10.8
Histidine*	His(H)		7.6

**Note :**

- \* Amino acids with an asterisk are essential amino acids, that must be supplemented through diet.
- † At pH = 7, Asp and Glu have a net negative charge and exist as anions. At pH = 7, Lys and Arg have a net positive charge and exist as cations. Rest of the amino acids at this pH exist in the neutral form.
- ‡ Structurally, in cystine, the two cysteine molecules are joined through sulfur (disulfide linkage).
- @@ Proline is an  $\alpha$ -imino acid, all amino acids are primary amines except proline and 4-hydroxyproline, which are 2° amines.
- @ Except Glycine all other amino acids are optically active.

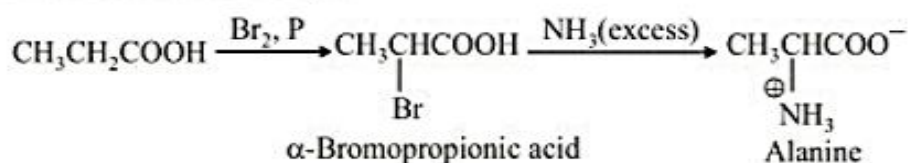
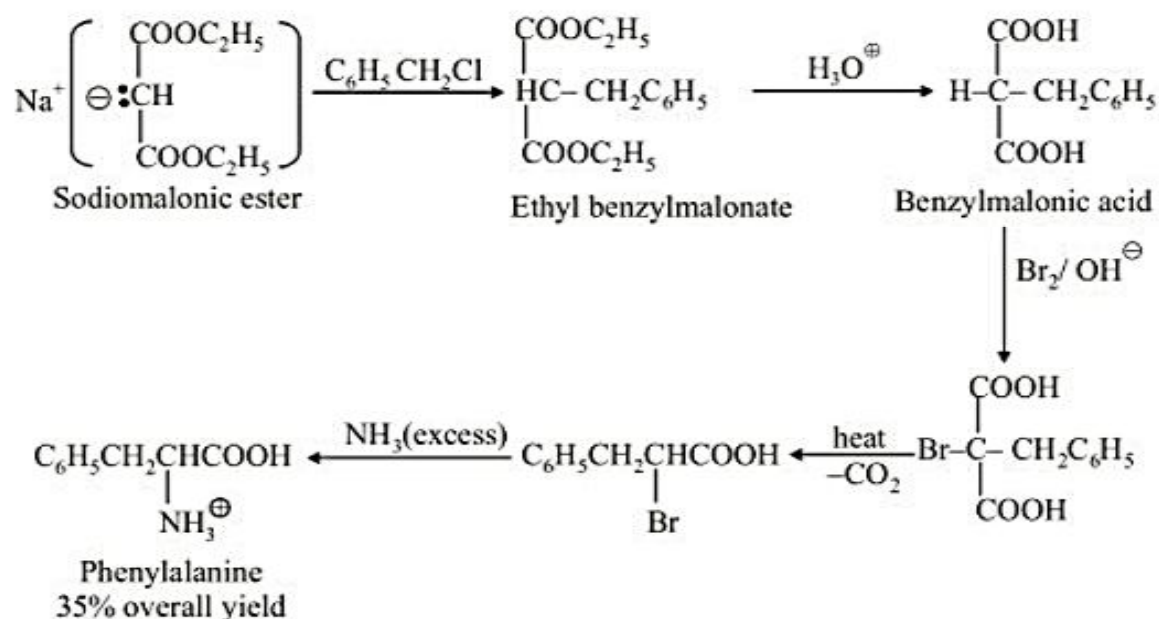
**Preparation of amino acids****(a) Gabriel Phthalimide synthesis**

Better yields are generally obtained by the gabriel phthalimide synthesis ; the  $\alpha$  - halo esters are used instead of  $\alpha$  - halo acids .

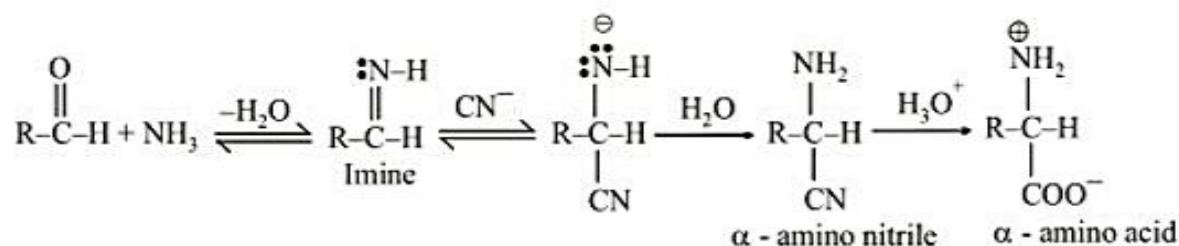


(b) **Amination of  $\alpha$  - Halo acids**

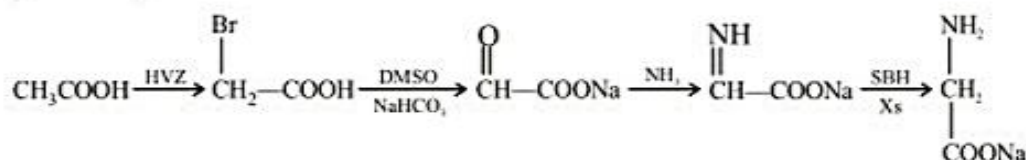
Sometimes an  $\alpha$  - chloro or  $\alpha$  - bromo acid is subjected to direct ammonolysis with a large excess of concentrated ammonia. For example,

(c) **From diethyl malonate**(d) **Strecker's synthesis**

Strecker's synthesis is also used for preparing  $\alpha$  - amino acids



In this reaction general aldehyde is treated with mixture of ammonium chloride and KCN in aqueous solution which forms  $\text{NH}_3$  and  $\text{HCN}$ ,  $\text{NH}_4\text{Cl} + \text{KCN} \xrightarrow{\text{aqueous}} \text{NH}_4\text{CN} + \text{KCl}$ ,  $\text{NH}_4\text{CN} \xrightarrow{\text{aqueous}} \text{NH}_3 + \text{HCN}$

(e) **Using KOOP synthesis**



## Properties of Amino acids

Although the amino acids are commonly shown as containing an amino group and a carboxyl group,  $\text{H}_2\text{NCHRCOOH}$ , certain properties, (both physical and chemical) are not consistent with this structure

### I. Physical properties

In contrast to amines and carboxylic acids, the amino acids are nonvolatile crystalline solids, which melt with decomposition at fairly high temperatures.

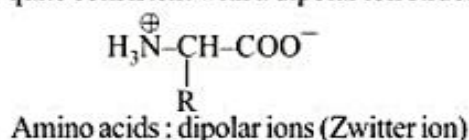
They are insoluble in non-polar solvents like petroleum ether, benzene or ether and are appreciably soluble in water.

Their aqueous solutions behave like solutions of substances of high dipole moment.

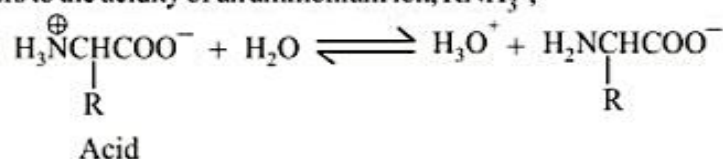
### Amino acids as dipolar ions

Acidity and basicity constant are ridiculously low for  $-\text{COOH}$  and  $-\text{NH}_2$  groups. Glycine, for example, has  $K_a = 1.6 \times 10^{-10}$  and  $K_b = 2.5 \times 10^{-12}$ , whereas most carboxylic acids have  $K_a$  values of about  $10^{-5}$  and most aliphatic amines have  $K_b$  values of about  $10^{-4}$ .

All these properties are quite consistent with a dipolar ion structure for the amino acids (I)

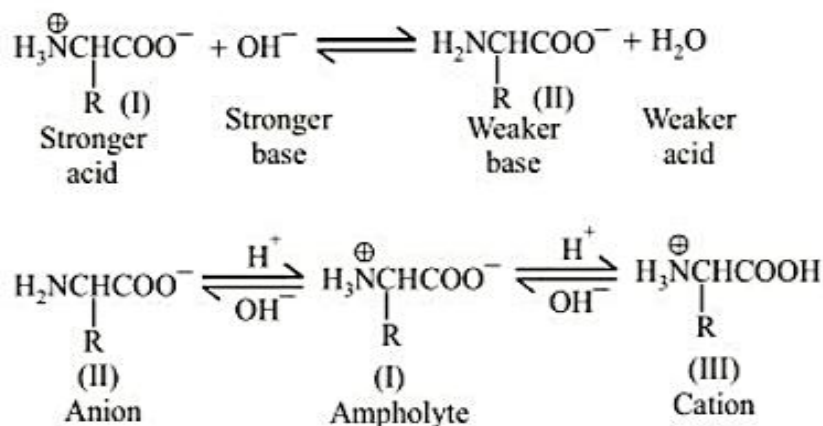


**Physical properties** - melting point, solubility, high dipole moment - are just what would be expected of such a salt. The acid-base properties also become understandable when it is realized that the measured  $K_a$  actually refers to the acidity of an ammonium ion,  $\text{RNH}_3^+$ ,



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{H}_2\text{NCHRCOO}^-]}{[\text{H}_3\text{N}^+\text{CHRCOO}^-]}$$

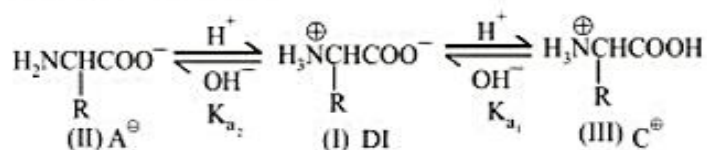
When the solution of an amino acid is made alkaline, the dipolar ion (I) is converted into the anion (II). The stronger base, hydroxide ion, removes a proton from the ammonium ion and displaces the weaker base, the amine.



Wherever feasible, we can speed up a desired reaction by adjusting the acidity or basicity of the solution in such a way as to increase the concentration of the reactive species.

### Isoelectric point of amino acids

What happens when a solution of an amino acid is placed in an electric field depends upon the acidity or basicity of the solution.



In quite alkaline solution, anions (II) exceed cations (III), and there is a net migration of amino acid toward the anode. In quite acidic solution, cations (III) are in excess, and there is a net migration of amino acid toward the cathode. If (II) and (III) are exactly balanced, there is no net migration; under such conditions any one molecule exists as a positive ion and as a negative ion for exactly the same amount of time, and any small movement in the direction of one electrode is subsequently cancelled by an equal movement back towards the other electrode. **The hydrogen ion concentration of the solution in which a particular amino acid does not migrate under the influence of an electric field is called the isoelectric point (pI) of that amino acid. The isoelectric point (pI) is the pH at which the amino acid exists only as a dipolar ion with net charge zero.**

For glycine, for example, the isoelectric point is at pH 6.1.

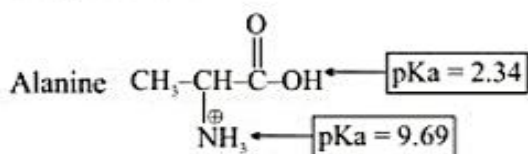
An amino acid usually shows its lower solubility in a solution at the isoelectric point, since here there is the highest concentration of the dipolar ion. As the solution is made more alkaline or more acidic, the concentration of one of the more soluble ions, (II) or (III) increases.

$$K_{a_1} = \frac{[\text{DI}][\text{H}^+]}{[\text{C}^+]}, \quad K_{a_2} = \frac{[\text{A}^-][\text{H}^+]}{[\text{DI}]} \quad \text{at pI } [\text{A}^-] = [\text{C}^+]$$

$$\frac{[\text{DI}][\text{H}^+]}{K_{a_1}} = \frac{K_{a_2}[\text{DI}]}{[\text{H}^+]} \qquad [\text{H}^+]^2 = K_{a_1} \times K_{a_2}$$

$$\text{on taking antilog pI} = \frac{\text{p}K_{a_1} + \text{p}K_{a_2}}{2}$$

The PI of an amino acid that does not have an ionizable side chain. (e.g. alanine), is midway between its two pKa values.

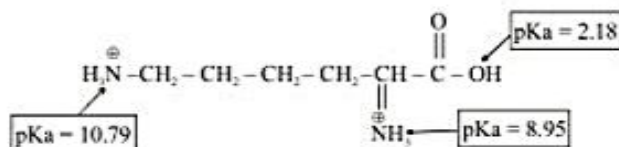


$$\text{pI} = \frac{2.34 + 9.69}{2} = \frac{12.03}{2} = 6.02$$

If an amino acid has an ionizable side chain, its PI is the average of the pKa values of the similarly ionizing groups (positive ionizing to uncharged or uncharged ionizing to negative.)

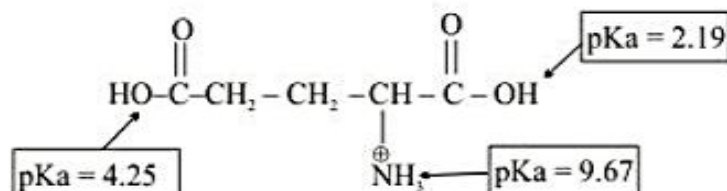
For example:

(i) Lysine



$$pI = \frac{10.79 + 8.95}{2} = \frac{19.74}{2} = 9.87$$

(ii) Glutamic acid



$$pI = \frac{2.19 + 4.25}{2} = \frac{6.44}{2} = 3.22$$

An amino acid having more COOH than NH<sub>2</sub> or more acidic COOH will have pI less than 7.

An amino acid having more –NH<sub>2</sub> than COOH or more basic –NH<sub>2</sub> will have pI more than 7.

Q. Write the structure of alanine at pH 2.5, 10.5 and 6.

### Electrophoresis

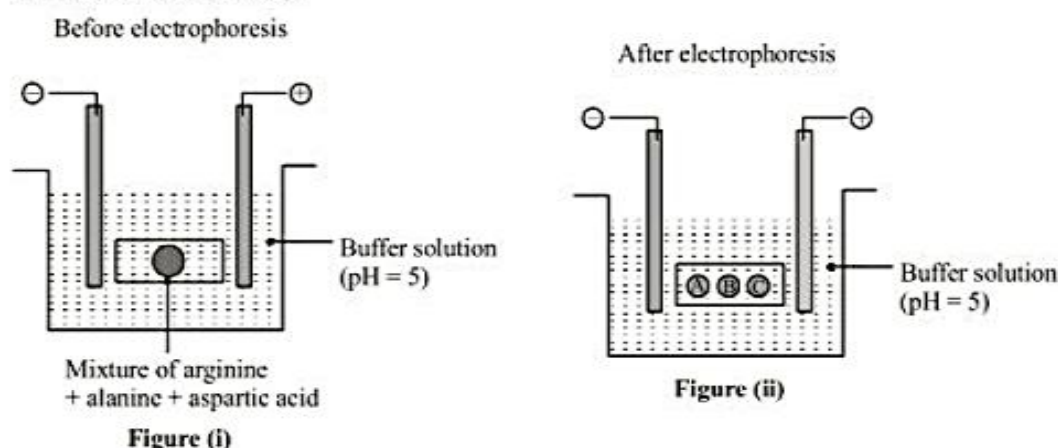
The movement of charged molecules (like amino acid) under the influence of an electric field is called electrophoresis. Electrophoresis separates amino acids on the basis of their pI values.

Amino acid is positively charged (moves towards cathode) if pH of the solution < pI

Amino acid is negatively charged (moves towards anode) if pH of the solution > pI

Q. How will you separate a ternary mixture of arginine, alanine & aspartic acid?

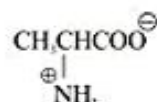
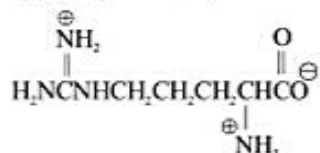
Ans. A few drops of a solution of an amino acid mixture are applied to the middle of a piece of filter paper. When the paper is placed in a buffer solution (pH = 5) between the two electrodes and an electric field is applied then arginine & alanine with pI > pH move towards the cathode and aspartic acid with pI < pH moves towards the anode. Out of arginine & alanine, alanine will move slowly towards the cathode due to lesser positive charge.



Ⓐ = arginine (pI = 10.76)

Ⓑ = alanine (pI = 6.02)

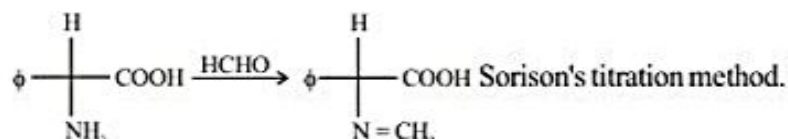
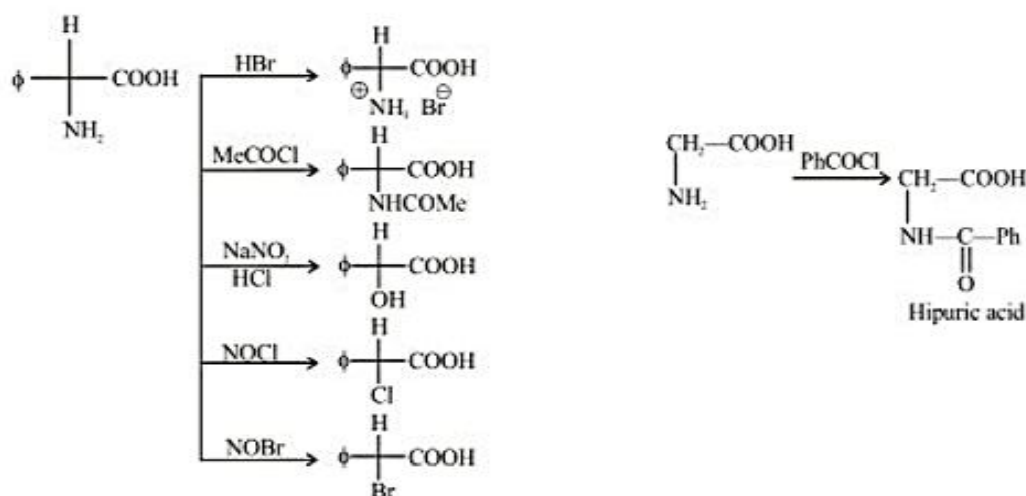
Ⓒ = aspartic acid (pI = 2.98)





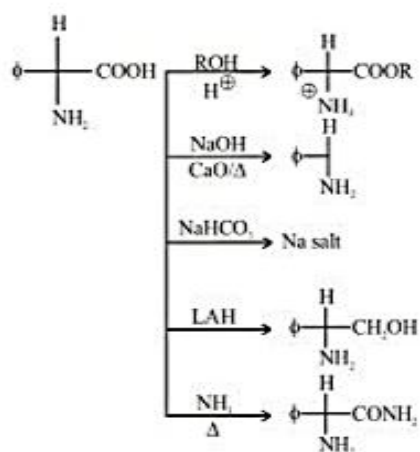
## General reactions of amino acids

### (1) Reactions due to $-NH_2$ group



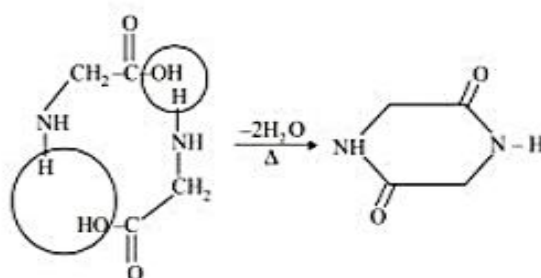
Reactions is used to block  $-NH_2$  group during volumetric analysis in.

### (2) Reactions due to $-COOH$ group.



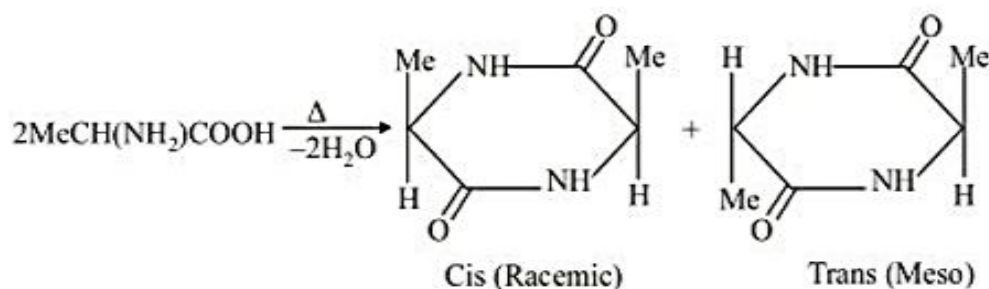
### (3) Heating Effect

(i) Heating of amino acids leads to intermolecular dehydration to form cyclic diamides.

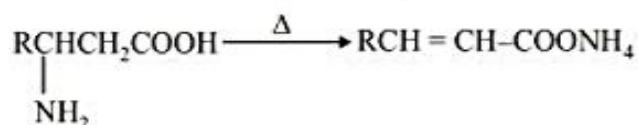




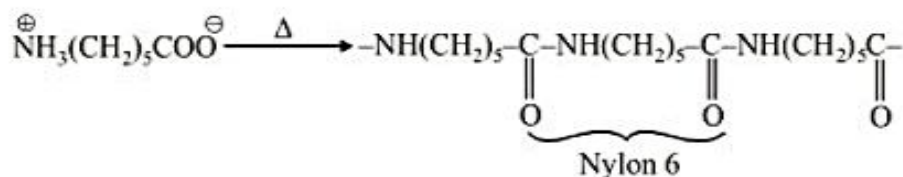
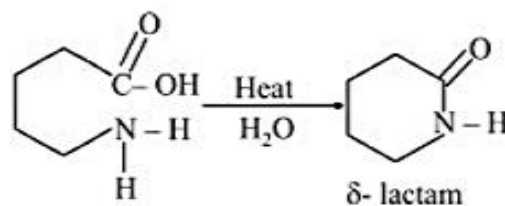
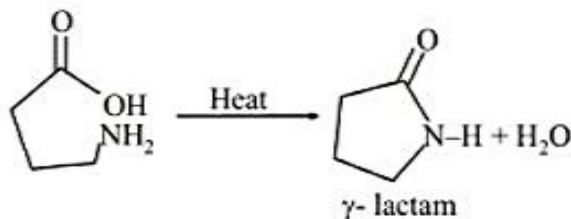
- (ii) When alanine is heated, then two diastereomers are obtained. One of them (trans) is not resolvable.



- (iii) When  $\beta$  - amino acids are heated,  $\alpha$ ,  $\beta$  - unsaturated salt are formed.



- (iv)  $\gamma, \delta, \epsilon$  - amino acids when heated alone gives  $\gamma, \delta$  - lactam and polymer respectively. The reason for the formation of polymer is that when  $\epsilon$  - amino cyclises intramolecularly, it leads to large angle strain within the compound



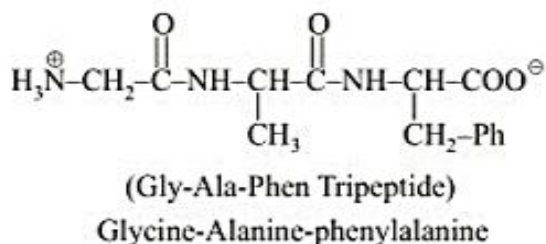
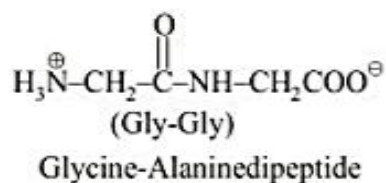
#### (4) Peptide

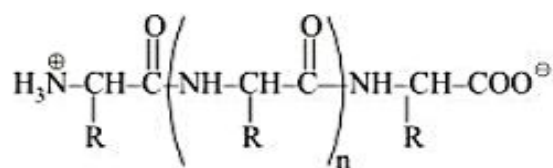
Peptides are amides formed by interaction between amino groups and carbonyl groups of amino acids.

The amino bonds  $\left( \begin{array}{c} -\text{NH}-\text{C}- \\ || \\ \text{O} \end{array} \right)$  that link amino acid residues are called peptide bonds. So peptide

bonds are the only covalent bonds that hold amino acid residues together in a peptide or protein.

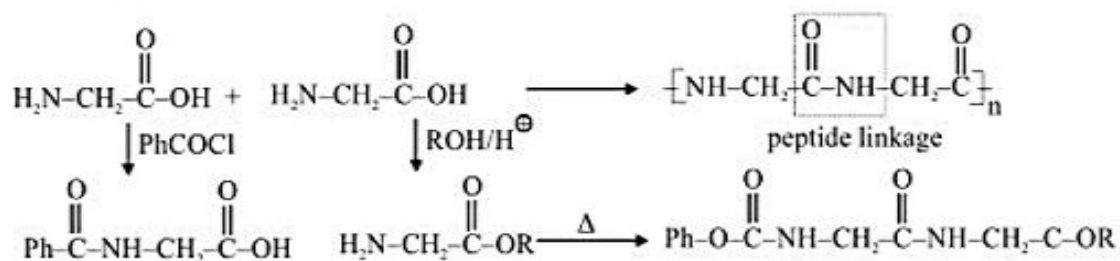
Depending upon the number of amino acid residues per molecule, they are known as dipeptides, tripeptides and so on and finally polypeptides. (By convention, peptides of molecular weight upto 1000 are known as polypeptides and above that as protein)





Polypeptide

Dipeptides are made from two amino acids where as oligopeptides are made from 3 to 10 amino acids. If 11 to 100 amino acids are present together they called polypeptide and 100 onwards they are called as macropeptide.

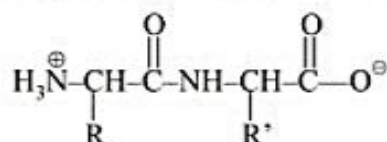


For the synthesis of polypeptides, the amino groups that are not to be linked in peptide bonds must be blocked so as to be unreactive. Then all other reactive functional groups must be protected to prevent their participation in the coupling produces. The coupling must be effected by a method that does not cause racemization or chemical alternation of the side chains.

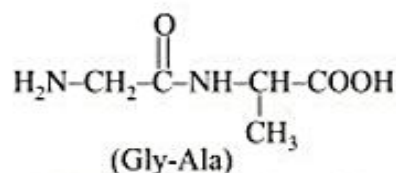
These type polyamide can be made only using part blocking technique.

Abbreviated name of amion acid with free  $\text{NH}_2$  is written first.

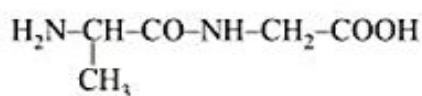
By convention peptide are written with the free amino group (the  $\text{--N--}$ terminal amino acid) on the left and the free carbonyl group (the  $\text{--C--}$  terminal amino acid) on the right.



For the nomenclature of peptides abbreviated name of amino acid with free  $\text{NH}_2$  group is written first. For example:

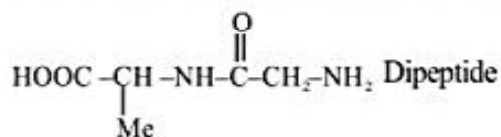


Glycine-Alanine-dipeptide

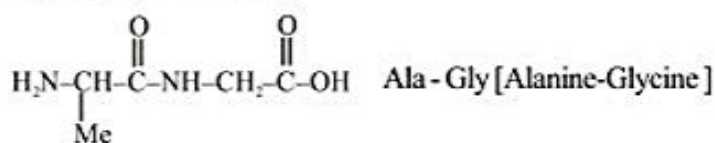


Alanine-Glycine-dipeptide

Polypeptide on hydrolysis give two amino acid are known as dipeptide



Gly Ala [Glycine Alanine]



Total number of polypeptide possible =  $X^n$

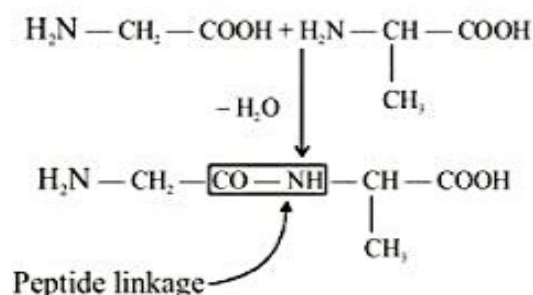
[X = type of amino acid interacting,  
n = number of amino acid molecule are interacting.]

- Q. Glycine can form how many Dipeptide? [Ans. One]  
 Q. Glycine can form how many Tripeptide? [Ans. One]  
 Q. Glycine and Ala can form how many Dipeptide? [Ans. Four]  
 Q. Gly, Ala, and Phenyl Ala can form how many Dipeptide? [Ans. Nine]  
 Q. Gly, Ala, can form how many Tripeptide? [Ans. Eight]

When Macropetide takes different shape due to intramolecular H - bonding between different layers is known as proteins

## Proteins

You have already read that proteins are the polymers of  $\alpha$ -amino acids and they are connected to each other by peptide bond or peptide linkage. Chemically, peptide linkage is an amide formed between  $\text{—COOH}$  group and  $\text{—NH}_2$  group. The reaction between two molecules of similar or different amino acids, proceeds through the combination of the amino group of one molecule with the carboxyl group of the other. This results in the elimination of a water molecule and formation of a peptide bond  $\text{—CO—NH—}$ . The product of the reaction is called a dipeptide because it is made up of two amino acids. For example, when carboxyl group of glycine combines with the amino group of alanine we get a dipeptide, glycylalanine.



Glycylalanine (Gly-Ala)

If a third amino acid combines to a dipeptide, the product is called a tripeptide. A tripeptide contains three amino acids linked by two peptide linkages. Similarly when four, five or six amino acids are linked, the respective products are known as tetrapeptide, pentapeptide or hexapeptide, respectively. When the number of such amino acids is more than ten, then the products are called polypeptides. A polypeptide with more than hundred amino acid residues, having molecular mass higher than 10,000u is called a protein. However, the distinction between a polypeptide and a protein is not very sharp. Polypeptides with fewer amino acids are likely to be called proteins they ordinarily have a well defined conformation of a protein such as insulin which contains 51 amino acids.

Proteins can be classified into two types on the basis of their molecular shape.

- (a) **Fibrous proteins :** When the polypeptide chains run parallel and are held together by hydrogen and disulphide bonds, then fibre-like structure is formed. Such proteins are generally insoluble in water. Some common examples are keratin (present in hair, wool, silk) and myosin (present in muscles), etc.
- (b) **Globular proteins :** This structure results when the chains of polypeptides coil around to give a spherical shape. These are usually soluble in water. Insulin and albumins are the common examples of globular proteins.

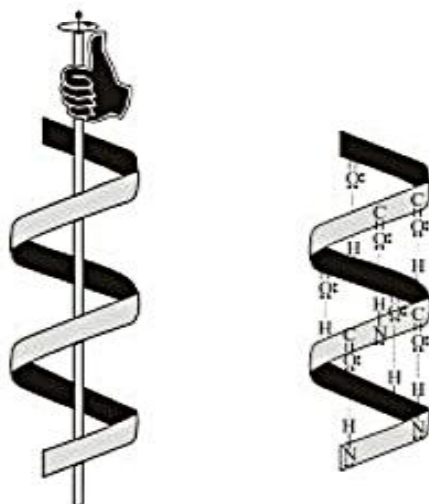


## Structure of Proteins

Structure and shape of proteins can be studied at four different levels, i.e., primary, secondary, tertiary and quaternary, each level being more complex than the previous one.

- (i) **Primary structure of proteins :** Proteins may have one or more polypeptide chains. Each polypeptide in a protein has amino acids linked with each other in a specific sequence and it is this sequence of amino acids that is said to be the primary structure of the protein. Any change in this primary structure i.e., the sequence of amino acids creates a different protein.
- (ii) **Secondary structure of proteins :** The secondary structure of protein refers to the shape in which a long polypeptide chain can exist. They are found to exist in two different types of structures viz.  $\alpha$ -helix and  $\beta$ -pleated sheet structure. These structures arise due to the regular folding of the backbone of the

polypeptide chain due to hydrogen bonding between  $\text{—}\overset{\text{O}}{\parallel}{\text{C}}\text{—}$  and  $\text{—NH—}$  groups of the peptide bond.

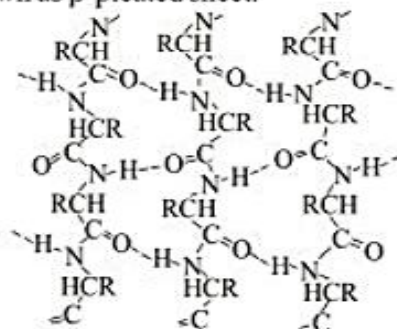


$\alpha$ -Helix structure of proteins

$\alpha$ -Helix is one of the most common ways in which a polypeptide chain forms all possible hydrogen bonds by twisting into a right handed screw (helix) with the  $\text{—NH}$  group of each amino acid residue

hydrogen bonded to the  $\text{>C=O}$  of an adjacent turn of the helix as shown in figure.

In  $\beta$ -structure all peptide chains are stretched out to nearly maximum extension and then laid side by side which are held together, by intermolecular hydrogen bonds. The structure resembles the pleated folds of drapery and therefore is known as  $\beta$ -pleated sheet.



$\beta$ -Pleated sheet structure of proteins



- (i) Ionic bonding : between  $\text{COO}^-$  and  $\text{NH}_3^+$  at different sites.
- (ii) H-bonding : mainly between side-chain  $\text{NH}_2$  and  $\text{COOH}$ , also involving OH's (Of serine, for example) and the N-H of tryptophan.
- (iii) Weakly hydrophobic Van der Waal's attractive forces engendered by side-chain R groups and
- (iv) Disulfide cross linkages between loops of the polypeptide chain.

The same kind of attractive and repulsive forces responsible for the tertiary structure operate to hold together and stabilize the subunits of the quaternary structure.

- (iii) **Tertiary structure of proteins :** The tertiary structure of proteins represents overall folding of the polypeptide chains i.e., further folding of the secondary structure. It gives rise to two major molecular shapes viz. fibrous and globular. The main forces which stabilise the  $2^\circ$  and  $3^\circ$  structures of proteins are hydrogen bonds, disulphide linkages, van der Waals and electrostatic forces of attraction.
- (iv) **Quaternary structure of proteins :** Some of the proteins are composed of two or more polypeptide chains referred to as sub-units. The spatial arrangement of these subunits with respect to each other is known as quaternary structure.

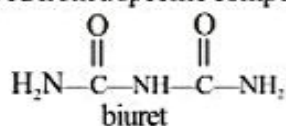
According to their biological action, they are classified as enzymes, hormones, antibodies, etc.

Protein found in living system with definite configuration and biological activity is termed as native protein. If a native protein is subjected to physical or chemical treatment, which may disrupt its higher structures (conformations) without affecting its primary structure, the protein is said to be denatured. During denaturation, the protein molecule uncoils from an ordered and specific conformation into a more random conformation leading to precipitation. Thus denaturation leads to increase in entropy and loss of biological activity of the protein. The denaturation may be reversible or irreversible. Thus, the coagulation of egg white on boiling of egg protein is an example of irreversible protein denaturation. However, in certain cases it is found that if the disruptive agent is removed the protein recovers its original physical and chemical properties and biological activity the reverse of denaturation is known as renaturation.

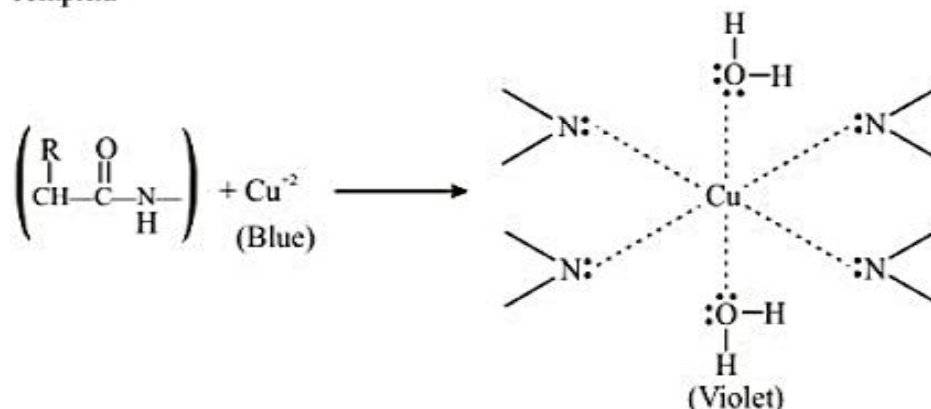
## TESTS OF PROTEINS

**Biuret test :** Addition of a very dilute solution of  $\text{CuSO}_4$  to an alkaline solution of a protein is done. A positive test is indicated by the formation of a pink violet to purple violet color.

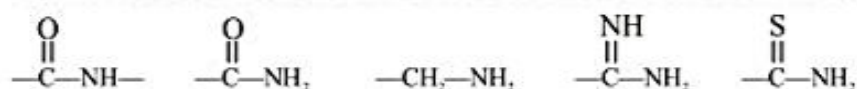
The name of test is derived from a specific compound, biuret, which gives a positive test with this reagent



When a protein reacts with copper (II) sulfate (blue), the positive test is the formation of a violet colored complex.

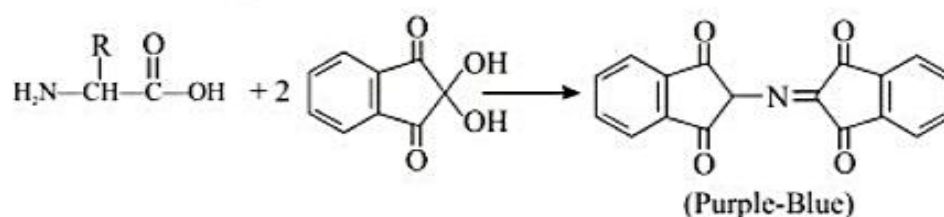


The biuret test works for any compound containing two or more of the following groups.



**Ninhydrin Test :** The ninhydrin test is a test for amino acids and proteins with a free  $-\text{NH}_2$  group. Amino acids are detected by ninhydrin test. All amino acids give violet - coloured product with ninhydrin (triketo hydroindene hydrate) except proline and 4 - hydroxy proline, which gives yellow colour with it.

When such an  $-\text{NH}_2$  group reacts with ninhydrin, a purple-blue complex is formed.



The same violet coloured dye forms from all  $\alpha$  - AA's with  $1^\circ$  amino groups because only their nitrogen is incorporated into it. The  $2^\circ$  amines proline and 4 - hydroxyproline give different adducts that absorb light at a different and thus have a different yellow colour.

## POLYMERS

The term polymer is used to describe a very large molecule that is made up of many repeating small molecular units. These small molecular units from which the polymer is formed are called monomers. The chemical reaction that joins the monomers together is called polymerisation. Starting from  $n$  molecules of a compound  $M$ , linking in a linear manner will form polymer  $x-M-(M)_{n-2}-M-y$ . The nature of linkages at the terminal units i.e.  $M-x$  and  $M-y$  depends upon the mode of reaction used in making the polymers.

### HOMOPOLYMERS AND COPOLYMERS

Polymers which are formed by only one type of monomer are called Homopolymers. Some examples of homopolymers and their monomers are given below:

Homopolymer	Monomer
Starch	Glucose
Cellulose	Glucose
Glycogen	Glucose
Dextrin	Glucose
Inulin	Fructose
Polyethylene	Ethylene
Polyvinyl chloride	Vinyl chloride
Teflon	Tetrafluoro ethylene
Nylon-6	Caprolactam
Polystyrene	Styrene
Orlon (Acrilan)	Acrylonitrile
Plexiglas (Lucite)	Methyl methacrylate
Teflon	Tetrafluoro ethylene
Nylon-6	Caprolactam
Polystyrene	Styrene
Orlon (Acrilan)	Acrylonitrile
Plexiglas (Lucite)	Methyl methacrylate
Polyvinyl acetate	Vinyl acetate

Polymers, which are formed by more than one type of monomers are known as copolymers. Some examples are given below in the table:

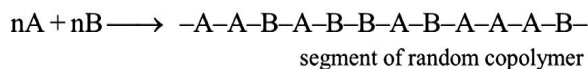
Copolymer	Monomers
Saran	Vinyl chloride and vinylidene chloride
SAN	Styrene and acrylonitrile
ABS	Acrylonitrile, butadiene and styrene
Butyl rubber	Isobutylene and Isoprene
Buna-S, SBR	Styrene and Butadiene
Buna-N, NBR	Acrylonitrile and Butadiene
Nylon-66	Hexamethylenediamine and Adipic acid
Terylene	Terephthalic acid and ethylene glycol

#### Types of copolymers

Depending upon the distribution of monomer units, the following types of copolymers are possible.

##### (1) Random Copolymer

If the monomer units have random distribution throughout the chain, it is called random copolymer. For example, if the monomer A and monomer B undergo copolymerisation then the structure of the random copolymer is





S.No.	Natural polymer	Monomers
1.	Polysaccharide	Monosaccharide
2.	Proteins	$\alpha$ -L-Amino acids
3.	Nucleic acid	Nucleotide
4.	Silk	Amino acids
5.	Natural Rubber (cis polyisoprene)	Isoprene (2-Methyl-1,3-butadiene)
6.	Gutta purcha (trans polyisoprene)	Isoprene



Natural polymers which take part in metabolic processes are known as biopolymers. Examples are polysaccharides, proteins, RNA and DNA.

**(2) Semisynthetic polymers**

Polymers which are prepared from natural polymers are known as semisynthetic polymers. Most of the semisynthetic polymers are prepared from cellulose. Examples are: cellulose acetate, cellulose nitrate, cellulose xanthate and Rayon.

**(3) Synthetic polymers**

Man-made polymers, i.e. polymers prepared in laboratory are known as synthetic polymers. Example are : PVC, polyethylene, polystyrene, nylon-6, nylon-66, nylon-610, terylene, synthetic rubbers etc.

**(II) CLASSIFICATION BASED UPON SHAPE**

**(1) Linear polymers**

Polymer whose structure is linear is known as linear polymer. The various linear polymeric chains are stacked over one another to give a well packed structure.



The chains are highly ordered with respect to one another. The structure is close packed in nature, due to which they have high densities, high melting point and high tensile (pulling) strength. Linear polymers can be converted into fibres.

**Note :**

(i) All fibers are linear polymers. Examples are cellulose, silk, nylon, terylene etc.

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**Note :**

(i) All fibers are linear polymers. Examples are cellulose, silk, nylon, terylene etc.

(ii) Linear polymers may be condensation as well as addition polymers. Examples are cellulose, polypeptide, nucleic acid, nylon, terylene etc.

**(2) Branched chain polymers**

Branched chain polymers are those in which the monomeric units constitute a branched chain. Due to the presence of branches, these polymers do not pack well. As a result branched chain polymers have lower melting points, low densities and tensile strength as compared to linear polymers.

Branched chain polymers may be formed due to addition as well as condensation polymerisation. Examples are amylopectin, glycogen, low density polyethylene and all vulcanised rubbers.



**(3) Cross-linked or Three Dimensional network polymers**

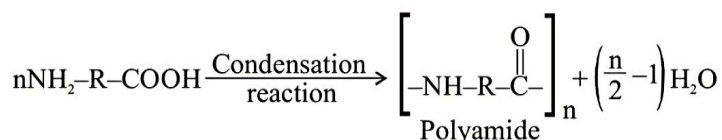
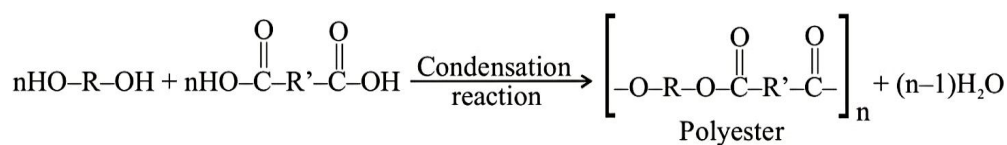
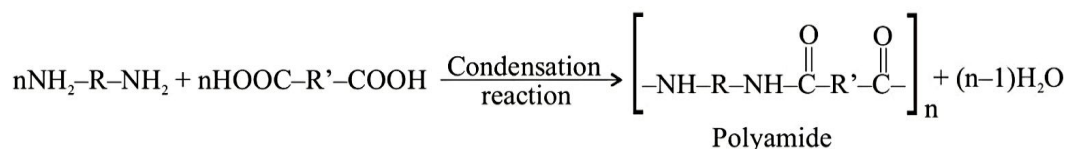
In these polymers the initially formed linear polymeric chains are joined together to form a three dimensional network structure. These polymers are hard, rigid and brittle. Cross-linked polymers are always condensation polymers. Resins are cross linked polymers.



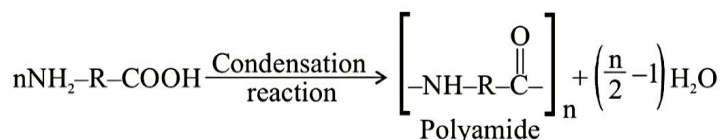
## CLASSIFICATION BASED UPON SYNTHESIS

### (1) Condensation polymerisation

- (i) They are formed due to condensation reactions.
- (ii) Condensation polymerisation is also known as step growth polymerisation.
- (iii) For condensation polymerisation, monomers should have at least two functional groups. Both functional groups may be same or different.
- (iii) Monomers having only two functional group always give linear polymer.  
For example,



- (iv) Condensation polymers do not contain all atoms initially present in the monomers. Some atoms are lost in the form of small molecules.

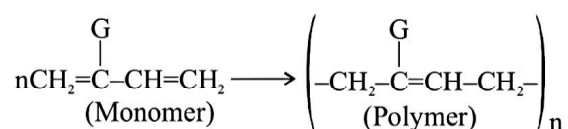


- (iv) Condensation polymers do not contain all atoms initially present in the monomers. Some atoms are lost in the form of small molecules.
- (v) Monomer having three functional groups always gives cross-linked polymer.  
Examples are : Urea-formaldehyde resin, phenol-formaldehyde resin.

### (3) Addition polymerisation

- (i) Polymers which are formed by addition reaction are known as addition polymers.
- (ii) If monomer is ethylene or its derivative, then addition polymer is either linear polymer of branch-chain polymer. Examples are : polystyrene, polytetrafluoroethylene, polyacrylonitrile etc.

- (iii) If monomer is 1, 3-butadiene or 2-substituted-1, 3-butadiene  $\left( \text{CH}_2 = \underset{\text{G}}{\text{C}} - \text{CH} = \text{CH}_2 \right)$ , then  
polymer is always branched chain polymer.

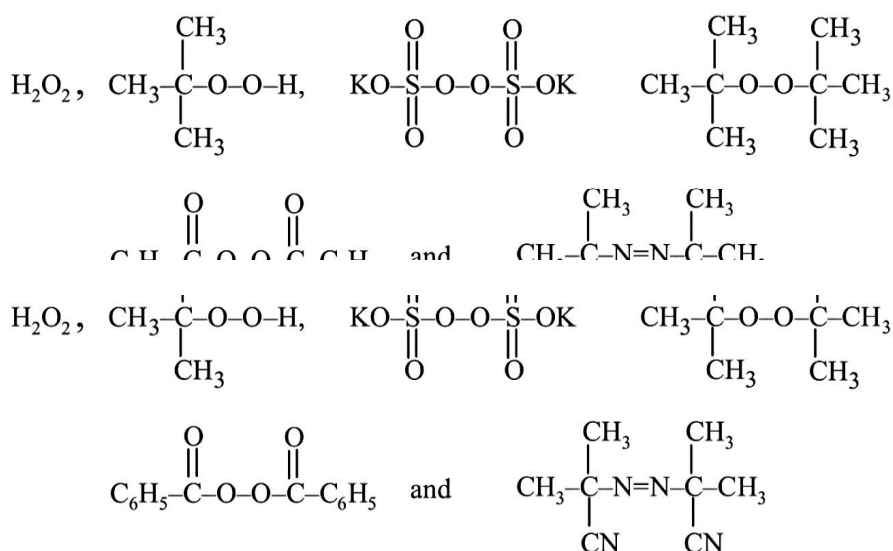


(Monomer)	(Polymer)
(i) G = H; 1,3 - Butadiene	(i) Polybutadiene
(ii) G=CH <sub>3</sub> ; 2 - Methyl-1, 3-butadiene or isoprene	(ii) Polyisoprene
(iii) G=Cl; 2 -Chloro-1, 3-butadiene or chloroprene	(ii) Pylchloroprene (Neoprene)
(iv) Addition polymers retain all the atoms of the monomer units in the polymer.	
(v) Addition polymerisation takes place in three steps : Initiation, chain propagation and chain termination.	
(vi) Addition polymers are called as chain growth polymers.	

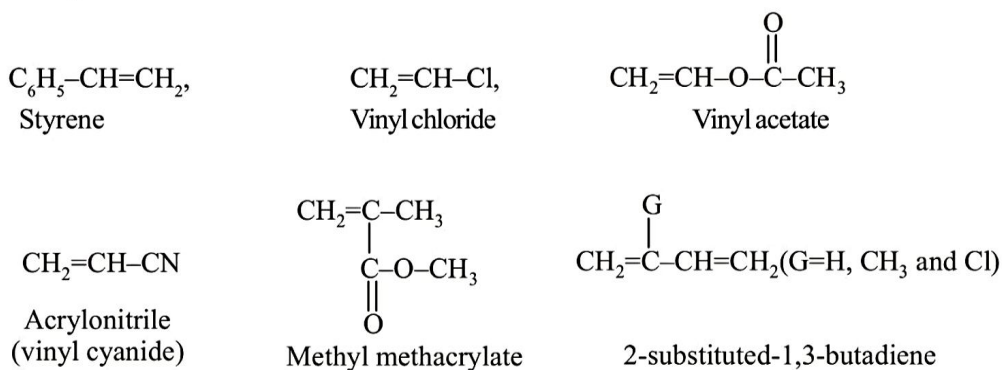
### Types of Addition Polymerisation

#### (A) Radical Polymerisation :

- (i) Radical polymerisation takes place in the presence of radical initiators. The radical initiator may be any of the following :



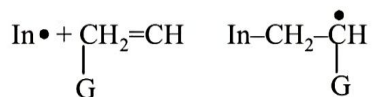
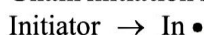
- (ii) Reaction intermediate of radical polymerization is a free radical.  
 (iii) Radical polymerization has more chance for those monomers whose free radicals are more stable.  
 Examples are :



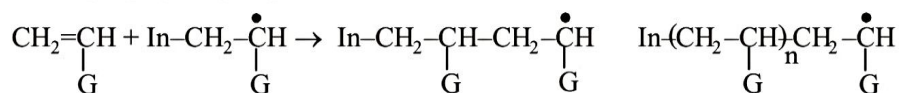
- (iv) Radical polymer has linear as well as branched chain structure  
 Most of the commercial addition polymers are vinyl polymers obtained from alkenes and their derivatives  $\text{CH}_2=\text{CH} \begin{array}{c} | \\ \text{G} \end{array}$  [G is H, C<sub>6</sub>H<sub>5</sub>, R etc.]

This type of polymerisation is performed by heating the monomer with only a very small amount of the initiator or by exposing the monomer to light. The general mode of radical polymerisation of vinyl monomers is depicted below :

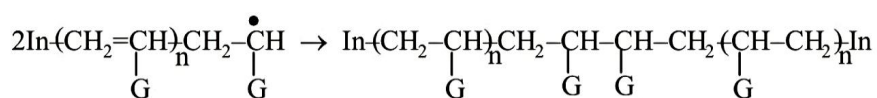
**Chain initiation step :**



**Chain propagating step :**



**Chain terminating step :**

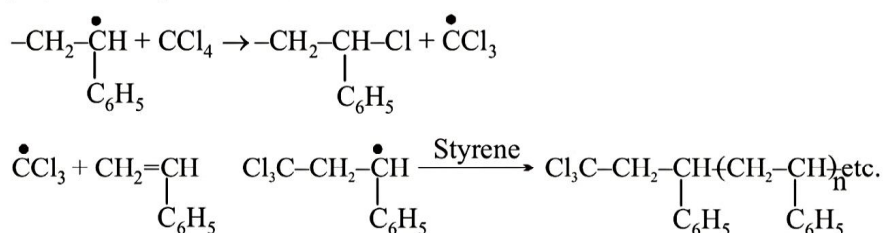


Polymer

In vinylic polymerisation, various other reaction of free radicals with some other compounds present may compete with the parent addition chain reactions. One such reaction takes place with molecules that can react with the growing chain to interrupt the further growth. This leads to the lowering of the average molecular mass of the polymer. Such reagents are called as chain transfer agents and include  $\text{CCl}_4$ ,  $\text{CBr}_4$  etc.

For example, in the presence of  $\text{CCl}_4$ , styrene polymerises to form polystyrene of a lower average molecular mass which also contains some chlorine what happens here is that growing polystyrene radical average molecular mass of the polymer. Such reagents are called as chain transfer agents and include  $\text{CCl}_4$ ,  $\text{CBr}_4$  etc.

For example, in the presence of  $\text{CCl}_4$ , styrene polymerises to form polystyrene of a lower average molecular mass which also contains some chlorine what happens here is that growing polystyrene radical which normally would add on a monomer reacts with the chain transfer agent to end the original chain and produces a new radical. The latter initiates a new polymerisation chain and thereby forms a new polymer as depicted below.



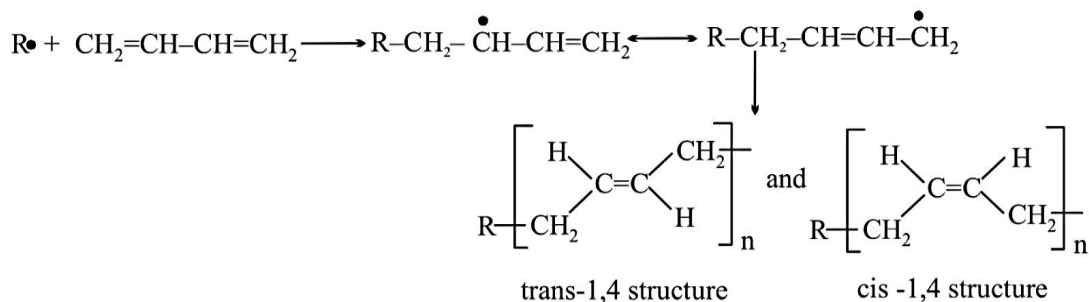
If the chain transfer agent a radical, which is highly unreactive, the reaction chain gets terminated such a compound thus inhibits or arrests polymerisation. Many amines, phenols, quinones etc. act as inhibitors. So, even traces of certain impurities, which can act as chain transfer agent or an inhibitor can interfere with the original polymerisation chain reaction. Hence, the monomers could be free from such inhibitors.

In case the alkene is a diene, the following kinds of polymerisation is possible :

**(1) 1,4 - polymerisation.**

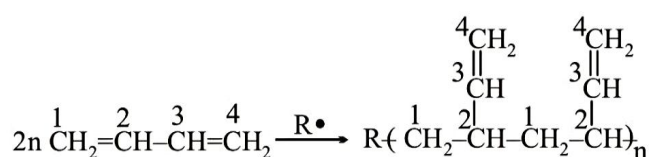
When the polymerisation takes place at  $\text{C}_1$  and  $\text{C}_4$  of butadiene, an unbranched polymer is formed. This product is different from that formed from an alkene having a double bond, which at each of its carbons is substituted by different groups and hence can exist either as trans-polybutadiene or cis-polybutadiene or a mixture as shown below.





## (2) 1,2-Polymerisation

Alternatively, 1,3-butadiene can undergo polymerisation at  $\text{C}_1$  and  $\text{C}_2$  to yield the polymeric product, polyvinylpolythene.



The double bonds in these initial polymers can be linked by further treatment with chemicals to modify the properties of the polymers. These reactions form the basis of the formation of rubber.

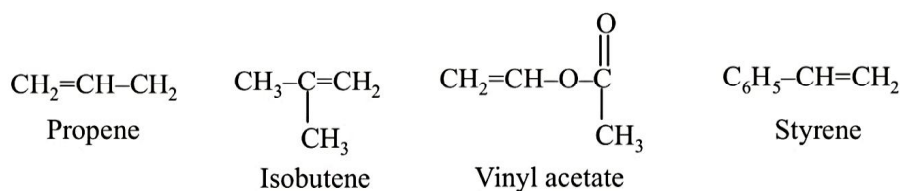
### (B) Cationic Polymerisation :

- Polymerisation which is initiated by an electrophile is known as cationic polymerisation.
- Reaction intermediate of cationic polymerisation is a carbocation.
- Carbocations can undergo rearrangement leading to the formation of a more stable carbocation.

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### (B) Cationic Polymerisation :

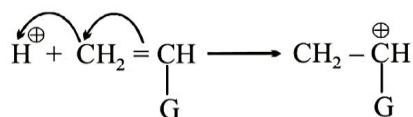
- Polymerisation which is initiated by an electrophile is known as cationic polymerisation.
- Reaction intermediate of cationic polymerisation is a carbocation.
- Carbocations can undergo rearrangement leading to the formation of a more stable carbocation.
- The electrophile commonly used for initiation is  $\text{BF}_3 \cdot \text{OEt}_2$ .
- Monomers that are best able to undergo polymerisation by a cationic mechanism are those with electron-donating substituents that can stabilise the carbocation. Some examples are :

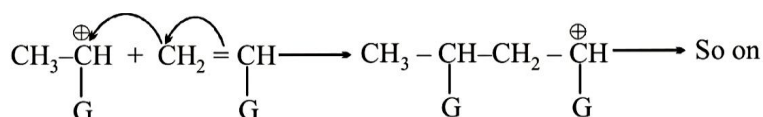
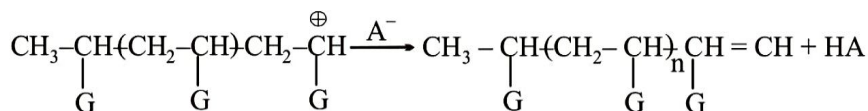


- It is terminated by a base.

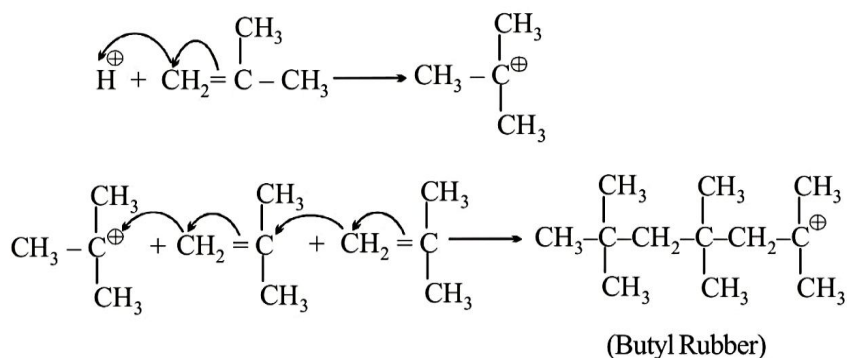
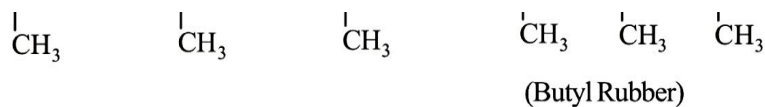
Thus, when the initiator is cationic in nature, it would generate a cationic intermediate on addition to the double bond for propagating the addition chain process and is termed as cationic addition polymerisation. The process is initiated by an acid. The stages of polymerisation are depicted below.

#### Chain initiation step :



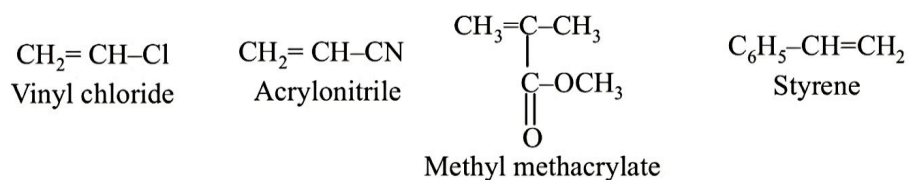
**Chain propagating step :****Chain terminating step :**

Cationic polymerisation is facilitated in monomers containing electron - releasing groups. Thus, isobutylene undergoes cationic polymerisation easily as it has two electron releasing  $-\text{CH}_3$  groups that will stabilize the intermediate carbo cation.

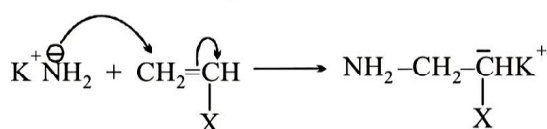
**(C) Anionic Polymerisation :****(C) Anionic Polymerisation :**

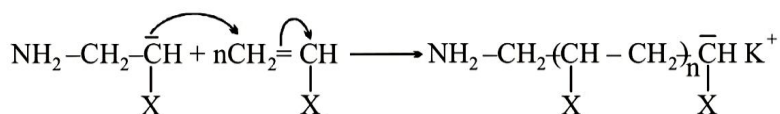
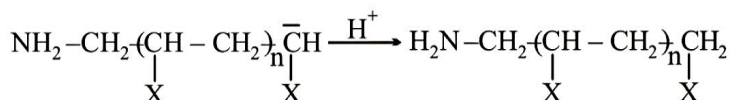
- (i) Anionic polymerisation takes place in the presence of base or nucleophile, which is initiator in this polymerization.
- (ii) Reaction intermediate in propagation steps are carboanion.
- (iii) The suitable initiator can be  $\text{NaNH}_2$  or  $\text{RLi}$ .
- (iv) Those monomers undergo anionic polymerisation reaction whose anion is stable.

Example of monomers are :



- (v) Anionic polymerisation always gives linear polymer.
- (vi) Anionic polymerisation terminated by an acid.  
The formation of polystyrene from styrene in the presence of potassium amide is an important example of this category of polymerisation. The mode of anionic polymerisation is depicted below :

**Chain initiation step :**

**Chain propagating step :****Chain terminating step :****(D) Ziegler- Natta polymerisation :**

- (i) Addition polymerisation which takes place in the presence of Ziegler- Natta catalyst  $[(\text{C}_2\text{H}_5)_3\text{Al}$  and  $\text{TiCl}_4]$  is known as Ziegler- Natta polymerisation or coordination polymerisation.
- (ii) Ziegler- Natta polymerisation always gives linear, stereo-regular polymers.
- (iii) Ziegler- Natta catalyst revolutionised the field of polymer chemistry because they allow the synthesis of stronger and stiffer polymers (due to linear geometry) that have greater resistance to cracking and heat. High density polyethylene is prepared using a Ziegler- Natta catalyst.

**CLASSIFICATION BASED ON INTERMOLECULAR FORCES (SECONDARY FORCES)**

- (i) Intermolecular forces present between polymeric chains are (a) Van der waals forces (b) Hydrogen bonds and (c) Dipole - dipole attractions.
- (ii) Mechanical properties such as tensile strength, elasticity, toughness etc. depend upon the secondary forces present between the polymeric chains.
- (iii) Magnitude of secondary forces depends upon the size of the molecule and the number of functional groups along the polymeric chains.

Magnitude of secondary forces is directly proportional to the length of the polymeric chain. On the basis of magnitude of secondary forces, polymers can be divided into the following **five categories**.

**(1) Elastomes**

An elastomer is a plastic that stretches and then reverts back to its original shape. It is randomly oriented amorphous polymer. It must have some cross-links so that the chains do not slip over one another. Very weak Van der waal forces are present in between polymeric chains.

When elastomers are stretched, the random chains stretch out, but there are insufficient Van der Waal forces to maintain them in that configuration and position. When the stretching force is removed, they go back to their random shape. Elastomers have the ability to stretch out over ten times their normal length. Important examples are vulcanized rubbers.

**Note :** Addition polymers obtained from butadiene and its derivatives are elastomers.

**(2) Fibres**

Fibres are linear polymers in which the individual chains of a polymer are held together by hydrogen bonds and / or dipole-dipole attraction. In the fibres, the polymeric chains are highly ordered with respect to one another.



Due to strong intermolecular forces of attraction and highly ordered geometry, fibres have high tensile strength and least elasticity. they have crystalline character and have high melting points and low solubility. Examples are cellulose, nylon, terylene, wool, silk etc.

**Note :**

- (i) Condensation polymers formed from bifunctional monomers are fibres in character.
- (ii) Addition polymers of alkene derivatives having strong- I group are fibres in character.

**(3) Thermoplastic Polymers**

Thermoplastic polymers are polymers that have both ordered crystalline regions (the regions of the polymer in which the chains are highly ordered with respect to one another) and amorphous, non crystalline regions (the regions of the polymer in which the chains are randomly oriented).

The intermolecular forces of attraction are in between elastomers and fibres. There are no cross-links between the polymeric chains. Thermoplastic polymers are hard at room temperature, but when they are heated, the individual chains can slip past one another and the polymer become soft and viscous. This soft and viscous material become rigid on cooling. The process of heating softening and cooling can be repeated as many times as desired without any change in chemical composition and mechanical properties of the plastic. As a result, these plastics can be moulded into toys, buckets, telephone and television cases. Some common examples are : polyethene polypropylene, polystyrene, polyvinyl chloride, teflon etc.

**Note :** Addition polymers obtained from ethylene and ethylene derivatives are thermoplastic polymers.

**(4) Thermosetting Polymers**

Polymers which become hard on heating are called thermosetting polymers. Thermosetting polymers

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**(4) Thermosetting Polymers**

Polymers which become hard on heating are called thermosetting polymers. Thermosetting polymers can be heated only once when it permanently sets into a solid, which cannot be remelted by heating.

Thermosetting polymers are cross- linked polymers . Greater the degree of cross - linking that exist, the more rigid is the polymer. Cross-linking reduces the mobility of the polymer chains, causing them to be relatively brittle materials. The hardening on heating is due to the extensive cross-linking between different polymer chains to give a three dimensional network solid. Examples are : phenol formaldehyde resin, urea-formaldehyde resin ,melamine - formaldehyde resin.

**DIFFERENCE BETWEEN THERMOPLASTIC AND THERMOSETTING POLYMERS**

S.No.	Thermoplastic polymers	Thermosetting polymers
1.	Soften and melt on heating and become hard on cooling i.e. process is reversible	Become hard on heating and process is irreversible.
2.	Can be moulded and remoulded and reshaped.	They can be moulded once and cannot be remoulded or reshaped.
3.	They are addition polymers	They are condensation polymers.
4.	Structure is generally linear	Structure is cross - linked.

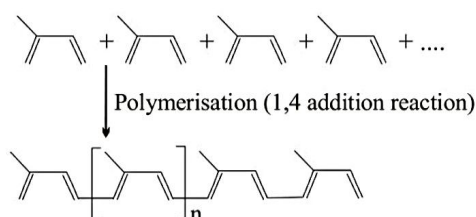


## RUBBER

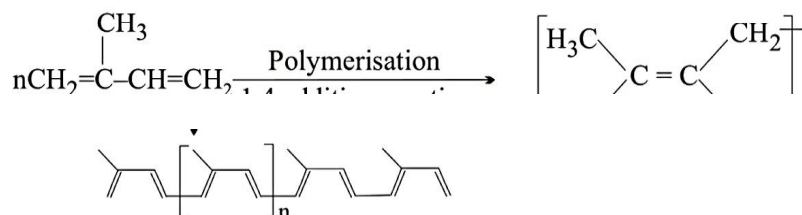
### 1. Natural Rubber

Natural rubber is obtained from nearly five hundred different plants but the main source is a brazilian tree. It is obtained in the form of milky sap known as latex. This latex is coagulated with acetic acid and formic acid. The coagulated mass is then squeezed.

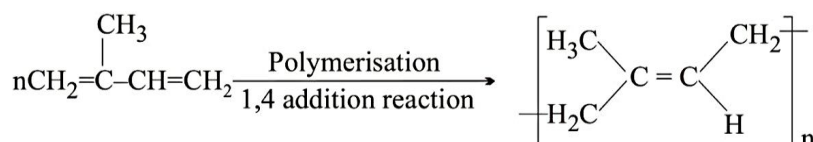
The raw natural rubber is a soft gummy and sticky mass. It is insoluble in water, dilute acids and alkalis but soluble in non-polar solvents. It has low elasticity and low tensile strength. Natural rubber is a polymer of 2-methyl-1, 3-butadiene (isoprene). On average, a molecule of rubber contains 5000 isoprene units held together by head to tail. All the double bonds in rubber are cis, hence natural rubber is cis-polyisoprene.



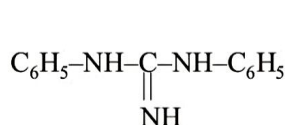
Gutta - percha is a naturally occurring isomer of rubber in which all the double bonds trans. Thus, gutta-percha is trans-polyisoprene.



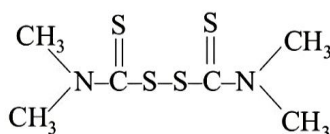
Gutta - percha is a naturally occurring isomer of rubber in which all the double bonds trans. Thus, gutta-percha is trans-polyisoprene.



It is harder and more brittle than rubber. It is the filling material that dentists use in root canal treatment. In order to give strength and elasticity to natural rubber, it is vulcanized. Heating of rubber with sulphur or sulphur containing compound at 150° C for few hours is known as vulcanisation. The essential feature of the vulcanisation is the formation of cross-linking between the polymeric chains. This cross-linking gives mechanical strength to the rubber. Vulcanisation process can be enhanced in the presence of certain organic compounds known as accelerators. The common accelerators are :



Diphenyl guanidine



Tetramethylthioureadisulph

In addition, fillers such as carbon black and zinc oxide are usually added to the crude rubber before vulcanisation in order to improve its wearing characteristics.

Natural rubber is used for making shoes, water - proof coats and golf balls. Vulcanised rubber is used for manufacture of rubber bands, gloves tubing and car tyres.

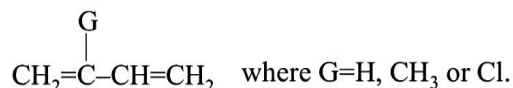
## SYNTHETIC RUBBER OR POLYMERISATION OF DIENES

Polymers of 1,3 - butadienes are called synthetic rubbers because they have some of the properties of natural rubbers including the fact that they are water proof and elastic.

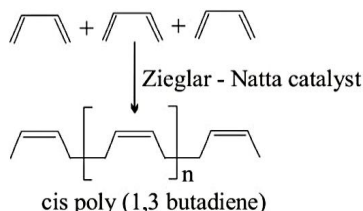
Synthetic rubbers have some improved properties. They are more flexible, tougher and more durable than natural rubber.

### 1. Homopolymers

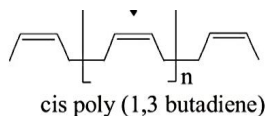
Monomer of this class is 2 - substituted - 1,3- butadienes.



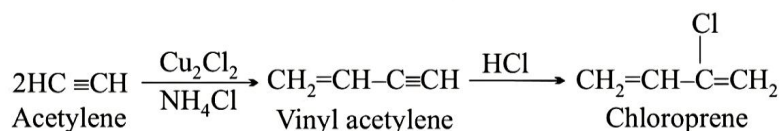
Polymerisation is always carried out in the presence of Ziegler-Natta catalyst which gives stereo regular polymers.



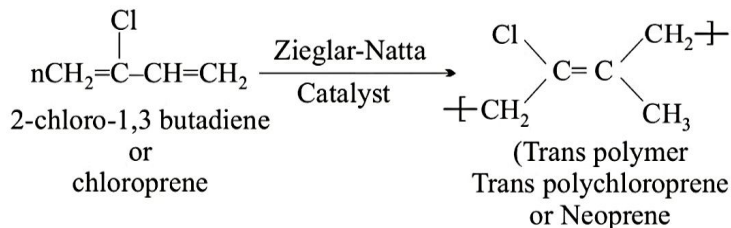
Neoprene was the first synthetic rubber manufactured on large scale. It is also called dieprene. Its monomer, chloroprene(2-chlorobutadiene) is prepared from acetylene.



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Chloroprene undergoes free radical polymerisation to form neoprene (polychloroprene).



Many of the properties of neoprene are similar to natural rubber but neoprene is more resistant to action of oils, gasoline and other hydrocarbons. It is also resistant to sunlight, oxygen, ozone and heat. It is non - inflammable.

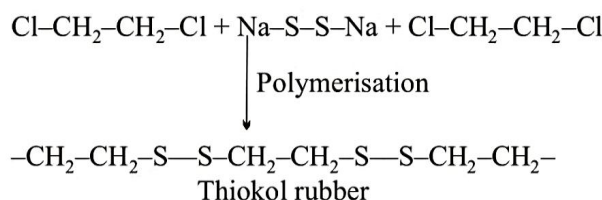
It is used for making automobile and refrigerator parts, hoses for petrol and oil containers, insulation of electric wires and conveyor belts.

### 2. Copolymers

The following synthetic rubbers are example of copolymers.

S.No.	Synthetic rubber	Monomers
1.	Buna-S, SBR (styrene-Butadiene rubber)	$\text{C}_6\text{H}_5\text{-CH=CH}_2$ (25%) + $\text{CH}_2=\text{CH-CH=CH}_2$ (75%)
2.	Buna-N, NBR (Nitrile-Butadiene rubber)	$\text{CH}_2=\text{CH-CN}$ (25%) + $\text{CH}_2=\text{CH-CH=CH}_2$ (75%)
3.	Butyl rubber	$\text{CH}_3\text{-C=CH}_2$ (98%) + Butadiene (2%)   $\text{CH}_3$
4.	ABS; Acrylonitrile, Butadiene, Styrene	$\text{CH}_2=\text{CH-CN}$ + $\text{CH}_2=\text{CH-CH=CH}_2$ + $\text{C}_6\text{H}_5\text{CH=CH}_2$

- (a) **Thiokol** : Thiokol is made by polymerising ethylene chloride and sodium polysulphide.



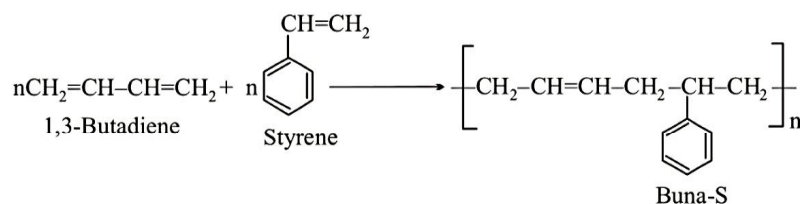
The repeating unit is  $\text{-CH}_2\text{-S-S-CH}_2\text{-}$

Thiokol is chemically resistant polymer. It is used in the manufacture of hoses and tank linings, engine gaskets and rocket fuel when mixed with oxidising agents.

-----  
The repeating unit is  $\text{-CH}_2\text{-S-S-CH}_2\text{-}$

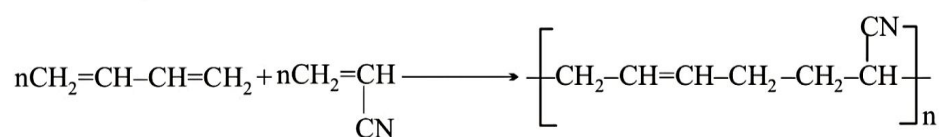
Thiokol is chemically resistant polymer. It is used in the manufacture of hoses and tank linings, engine gaskets and rocket fuel when mixed with oxidising agents.

- (b) **Buna -S (SBR : Styrene-butadiene rubber)** : Buna-S rubber is a copolymer of three moles of butadiene and one mole of styrene. In Buna-S, 'Bu' stands for butadiene, 'na' for symbol of sodium (Na) which is a polymerizing agent and 'S' stands for styrene. It is an elastomer (General purpose styrene Rubber or GRS).



Buna-S is generally compounded with carbon black and vulcanised with sulphur. It is extremely resistant to wear and tear and therefore used in the manufacture of tyres and other mechanical rubber goods. It is obtained as a result of free radical copolymerisation of its monomers.

- (c) **Buna-N** : It is obtained by copolymerisation of butadiene and acrylonitrile (General purpose Rubber acrylonitrile or GRA).



It is very rigid and is very resistant to action of petrol, lubricating oil and many organic solvents. It is mainly used for making fuel tanks.



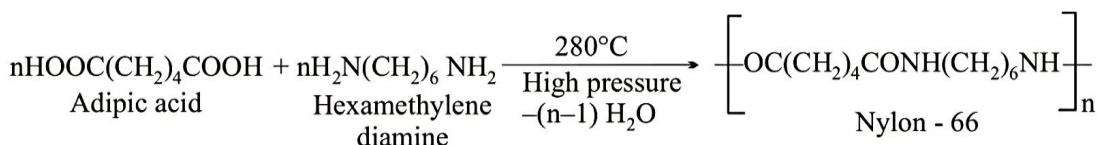
- (d) **Cold Rubber** : Cold rubber is obtained by polymerisation of butadiene and styrene at  $-18^{\circ}$  to  $5^{\circ}\text{C}$  temperature in the presence of redox system. Cold rubber has a greater tensile strength and greater resistance to abrasion than SBR.

## NYLON

Nylon is used as a general name for all synthetic fibres forming polyamides, i.e., having a protein like structure. A number is usually suffixed with the name 'nylon' which refers to the number of carbon atoms present in the monomers.

### (1) NYLON - 66 (Nylon six, six)

It is obtained by the condensation polymerisation of hexamethylenediamine (a diamine with six carbon atoms) and adipic acid (a dibasic acid having 6 carbon atoms).



### (2) NYLON-610 (Nylon six, ten)

It is obtained by condensation polymerisation of hexamethylenediamine (six carbon atoms) and sebacic acid (a dibasic acid with 10 carbon atoms.)

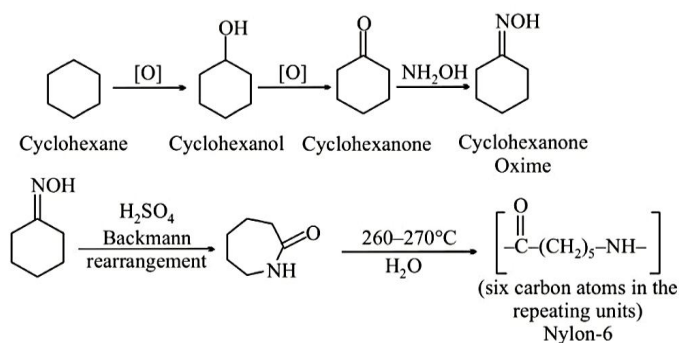
Nylon fibres are stronger than natural fibres and so are used in making cords and ropes. The fibres are elastic, light, very strong and flexible. They have drip dry property and retain creases. It is inert towards chemicals and biological agents. It can be blended with wool. Nylon fibres are used in making garments, carpets, fabrics, tyre cords, ropes, etc.

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### (3) NYLON-6 (Perlon L)

A polyamide closely related to nylon is known as perlon L (Germany) or Nylon - 6 (USA). It is prepared by prolonged heating of caprolactam at  $260-270^{\circ}\text{C}$ . It is formed by self condensation of a large number of molecules of amino caproic acid. Since, caprolactam is more easily available, it is used for polymerization, with is carried out in the presence of  $\text{H}_2\text{O}$  that first hydrolyses the lactam to amino acid. Subsequently, the amino acid can react with the lactam and the process goes on and onto form the polyamide polymer.

Caprolactam is obtained by Backmann rearrangement of cyclohexanone oxime.



### (4) NYLON-2-NYLON-6

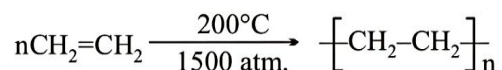
It is an alternating polyamide copolymer of glycine and amino caproic acid and is biodegradable.



## POLYETHYLENE

Polyethylene is of two types :

- (a) **Low Density Poly Ethylene (LDPE)** : It is manufactured by heating ethylene at 200°C under a pressure of 1500 atmospheres and in the presence of traces of oxygen. This polymerisation is a free radical polymerisation.



The polyethylene produced has a molecular mass of about 20,000 and has a branched structure. Due to this, polyethylene has a low density (0.92) and low melting point (110°C). That is why polyethylene prepared by free radical polymerisation is called low density polyethylene. It is a transparent polymer of moderate tensile strength and high toughness. It is widely used as a packing material and as insulation for electrical wires and cables.

- (b) **High Density Poly Ethylene (HDPE)** : It is prepared by the use of Ziegler - Natta catalyst at 160°C under pressure of 6 to 7 atmosphere.

The polymer is linear chain, hence it has high density (0.97) and has high melting point (130°C). That is why it is called high density polyethylene. It is a translucent polymer. It has greater toughness, hardness and tensile strength than low density polyethylene. It is used in the manufacture of containers (buckets, tubes), house wares, bottles and toys.

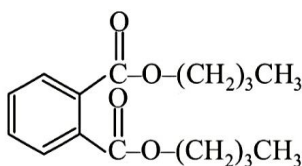
## PLASTICISER

A plasticiser is an organic compound that dissolves in the polymer and allows the polymer chains to slide

and tensile strength than low density polyethylene. It is used in the manufacture of containers (buckets, tubes), house wares, bottles and toys.

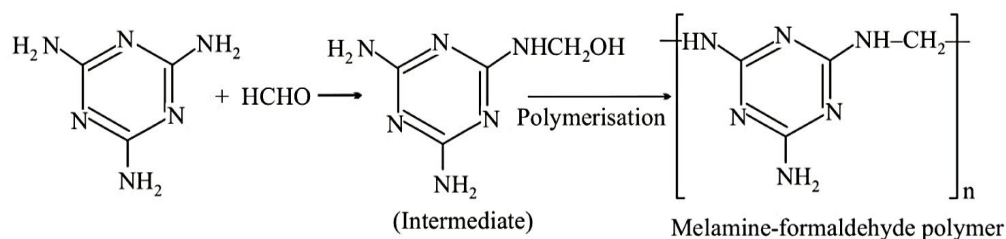
## PLASTICISER

A plasticiser is an organic compound that dissolves in the polymer and allows the polymer chains to slide past one another. This makes polymer more flexible. Dibutylphthalate is a commonly used plasticiser.



## MELAMINE - FORMALDEHYDE RESIN

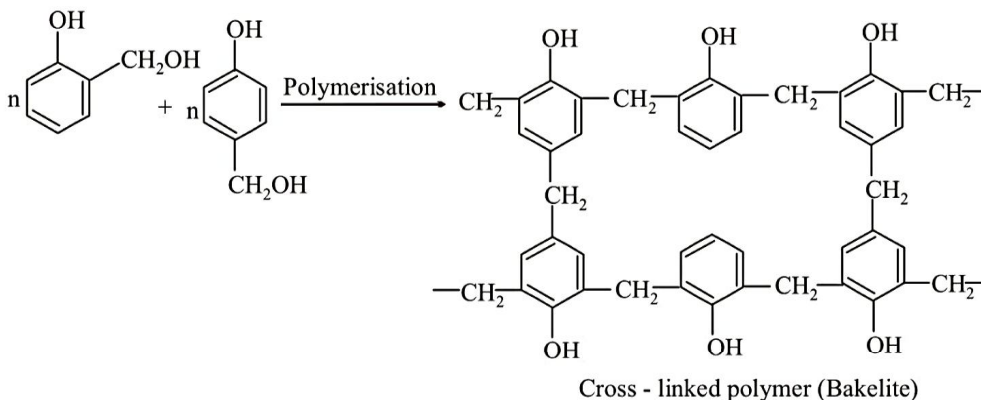
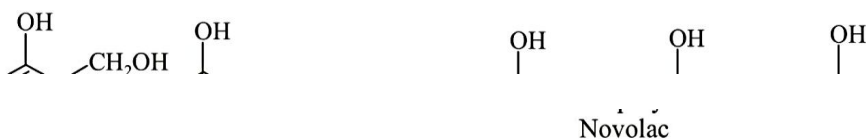
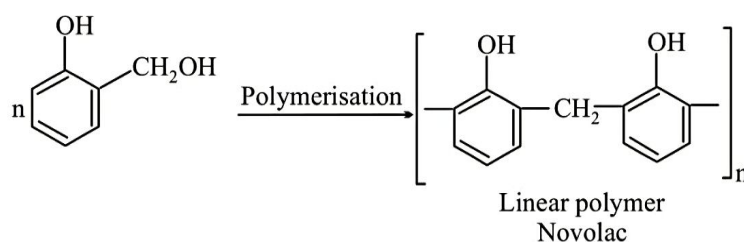
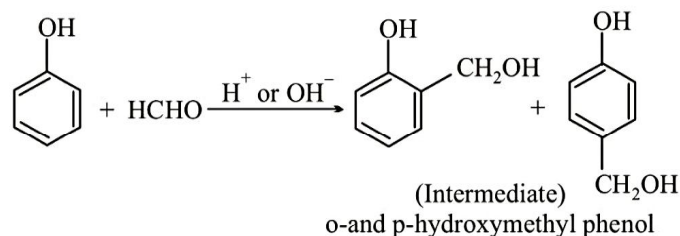
This resin is formed by condensation polymerisation of melamine and formaldehyde.



It is a quite hard polymer and is used widely for making plastic crockery under the name melamine. The articles made from this polymer do not break even when dropped from considerable height.

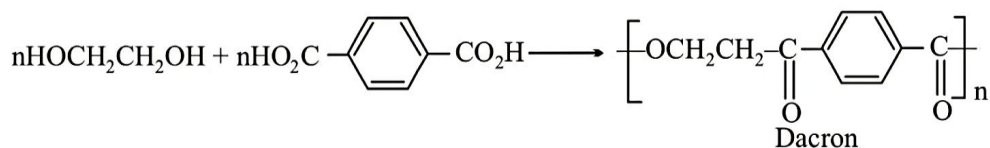
## BAKELITE

Phenol-formaldehyde resins are obtained by the reaction of phenol and formaldehyde in the presence of either an acid or a basic catalyst. The reaction starts with the initial formation of ortho and para-hydroxymethyl phenol derivatives, which further react with phenol to form compounds where rings are joined to each other with  $-\text{CH}_2-$  groups. The reaction involves the formation of methylene bridges in ortho, para or both ortho and para positions. Linear or cross-linked materials are obtained depending on the conditions of the reaction.



## POLYESTERS

Dacron is a common polyester, prepared using ethylene glycol and terephthalic acid. The reaction is carried out at  $140^\circ$  to  $180^\circ \text{C}$  in the presence of zinc acetate and  $\text{Sb}_2\text{O}_3$  as catalyst.



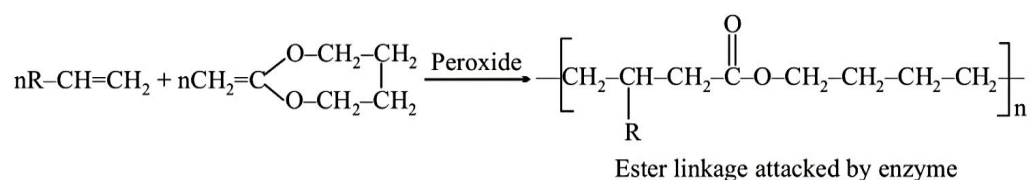
The terylene fibre (Dacron) is crease resistant and has low moisture absorption. It has high tensile strength. It is mainly used in making wash and wear garments, in blending with wool to provide better crease and wrinkle resistance.

## BIODEGRADABLE POLYMERS

By far the largest use of synthetic polymers is as plastic. A major portion of it is used as throwaway containers and packing materials. Since plastics do not disintegrate by themselves, they are not biodegradable over a period of time. Non - biodegradability is due the carbon-carbon bonds of addition polymers which are inert to enzyme catalysed reaction. These polymers create pollution problem.

Biodegradable polymers are the polymers that can be broken into small segments by enzyme catalysed reactions using enzymes produced by microorganisms. In biodegradable polymers, bonds that can be broken by the enzymes are inserted into the polymers. Therefore, when they are buried as waste, enzymes present in the ground can degrade the polymer.

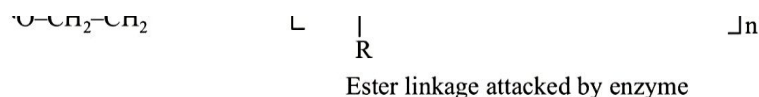
One method involves inserting hydrolysable ester group into the polymer. For example, when acetal (I) is added during the polymerization of alkene, ester group is inserted into the polymeric chains.



Aliphatic polyesters are important class of biodegradable polymers. Some examples are described below:

(1) **Poly - Hydroxybutyrate-CO-β-Hydroxyvalerate (PHBV)**

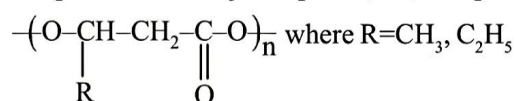
It is a copolymer of 3 - hydroxybutanoic acid and 3 hydroxypentanoic acid, in which the monomer units



Aliphatic polyesters are important class of biodegradable polymers. Some examples are described below:

(1) **Poly - Hydroxybutyrate-CO-β-Hydroxyvalerate (PHBV)**

It is a copolymer of 3 - hydroxybutanoic acid and 3 hydroxypentanoic acid, in which the monomer units are connected by ester linkages.



The properties of PHBV vary according to the ratio of both the acids. 3-Hydroxybutanoic acid provides stiffness and 3-hydroxypentanoic acid imparts flexibility to the co-polymer. It is used in specialty packaging, orthopaedic devices and even in controlled drug release. When a drug is put in a capsule of PHBV, It is released only after the polymer is degraded. PHBV also undergoes bacterial degradation in the environment.

(2) **Poly (Glycolic Acid) And Poly (Lactic Acid)**

They constitute commercially successful biodegradable polymers such as sutures. Dextron was the first bioadsorbable suture made for biodegradable polyesters for post - operative stitches.

## MOLECULAR MASS OF POLYMER

Normally, a polymer contains chains of varying lengths and therefore, its molecular mass is always expressed as an average. In contrast, natural polymers such as protein contains chain of identical length and hence, have definite molecular mass.

The molecular mass of a polymer is expressed as

- (a) Number average molecular mass ( $\overline{M}_n$ )

$$\overline{M}_n = \frac{\sum N_i M_i}{\sum N_i}$$

where  $N_i$  is the number of molecules of molecular mass  $M_i$

- (b) Weight average molecular mass ( $\overline{M}_w$ )

$$\overline{M}_w = \frac{\sum N_i M_i^2}{\sum N_i M_i}$$

where  $N_i$  is the number of molecules of molecular mass  $M_i$ . Methods such as light scattering and ultracentrifuge depend on the mass of the individual molecules and yield weight average molecular masses.  $\overline{M}_n$  is determined by employing methods which depend upon the number of molecules present in the polymer sample viz. colligative properties like osmotic pressure.

The ratio of the weight and number average molecular masses ( $\overline{M}_w / \overline{M}_n$ ) is called Poly Dispersity Index (PDI). Some natural polymers, which are generally monodispersed, the PDI is unity (i.e.  $\overline{M}_w = \overline{M}_n$ ).

In synthetic polymers, which are always polydispersed,  $PDI > 1$  because  $\overline{M}_w$  is always higher than  $\overline{M}_n$ .

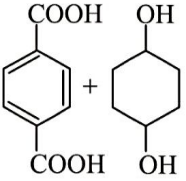
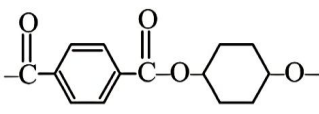
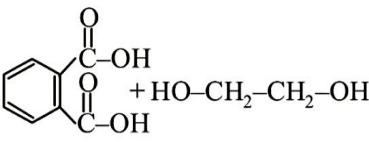
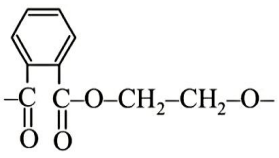
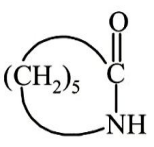
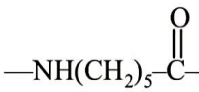
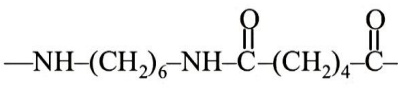
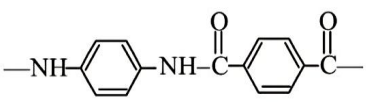
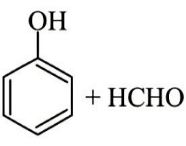
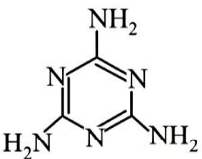
IVLn.

## COMMON POLYMERS

	Monomer	Repeating unit	Polymer
1.	$\text{CH}_2=\text{CH}_2$ Ethylene	$-\text{CH}_2-\text{CH}_2-$	Polyethylene
2.	$\text{CH}_3-\text{CH}=\text{CH}_2$ Propene	$\begin{array}{c} \text{CH}_3 \\   \\ -\text{CH}_2-\text{CH}- \end{array}$	Polypropene
3.	$\text{C}_6\text{H}_5-\text{CH}=\text{CH}_2$ Styrene	$\begin{array}{c} -\text{CH}_2-\text{CH}- \\   \\ \text{C}_6\text{H}_5 \end{array}$	Polystyrene
4.	$\text{CF}_2=\text{CF}_2$ Tetrafluoroethylene	$-\text{CF}_2-\text{CF}_2-$	Polytetrafluoroethylene (PTFE), Teflon
5.	$\text{CH}_2=\text{CH}-\text{Cl}$ Vinyl chloride	$\begin{array}{c} \text{Cl} \\   \\ -\text{CH}_2-\text{CH}- \end{array}$	Polyvinyl Chloride (PVC)
6.	$\text{CH}_2=\text{CH}-\text{CN}$ Vinyl cyanide or Acrylonitrile	$\begin{array}{c} \text{CN} \\   \\ -\text{CH}_2-\text{CH}- \end{array}$	Polyvinyl cyanide, polyacrylonitrile, Orlon.



7.	$\begin{array}{c} \text{H}_3\text{C} \quad \text{O} \\   \quad    \\ \text{CH}_2=\text{C}-\text{C}-\text{O}-\text{CH}_3 \\ \text{Methyl methacrylate} \end{array}$	$\begin{array}{c} \text{COOCH}_3 \\   \\ -\text{CH}_2-\text{C}- \\   \\ \text{CH}_3 \end{array}$	Polymethyl methacrylate, Plexiglas, Lucite
8.	$\begin{array}{c} \text{O} \\    \\ \text{CH}_2=\text{CH}-\text{O}-\text{C}-\text{CH}_3 \\ \text{Vinyl acetate} \end{array}$	$\begin{array}{c} \text{OCOCH}_3 \\   \\ -\text{CH}_2-\text{CH}- \end{array}$	Polyvinyl Acetate
9.	$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$ 1,3-butadiene	$-\text{CH}_2-\text{CH}-\text{CH}-\text{CH}_2-$	Polybutadiene, Buna rubber
10.	$\begin{array}{c} \text{CH}_2=\text{CH}-\text{Cl} \text{ (vinyl chloride)} \\ + \\ \text{CH}_2=\text{CCl}_2 \text{ (Vinylidene chloride)} \end{array}$	$\begin{array}{c} \text{Cl} \\   \\ -\text{CH}_2-\text{CH}-\text{CCl}_2-\text{CH}_2- \end{array}$	Saran
11.	$\begin{array}{c} \text{C}_6\text{H}_5-\text{CH}=\text{CH}_2 \text{ (Styrene)} \\ + \\ \text{CH}_2=\text{CH}-\text{CN} \text{ (acrylonitrile)} \end{array}$	$\begin{array}{c} \text{C}_6\text{H}_5 \quad \text{CN} \\   \quad   \\ -\text{CH}_2-\text{CH}-\text{CH}-\text{CH}_2- \end{array}$	SAN
12.	$\text{CH}_2=\text{CH}-\text{CN} + \text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$	—	ABS
13.	$\begin{array}{c} + \\ \text{C}_6\text{H}_5-\text{CH}=\text{CH}_2 \\ \text{CH}_2=\text{C}-\text{CH}_2 + \text{CH}_2=\text{C}-\text{CH}=\text{CH}_2 \\   \quad   \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$	—	Butyl rubber
14.	$\text{C}_6\text{H}_5-\text{CH}=\text{CH}_2 + \text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$	—	Buna -S, SBR
15.	$\text{CH}_2=\text{CH}-\text{CN} + \text{C}_6\text{H}_5-\text{CH}=\text{CH}_2$	—	Buna-N, NBR
16.	$\begin{array}{c} \text{Cl} \\   \\ \text{CH}_2=\text{C}-\text{CH}=\text{CH}_2 \\ \text{Chloroprene} \end{array}$	$\begin{array}{c} \text{Cl} \\   \\ -\text{CH}_2-\text{C}=\text{CH}-\text{CH}_2- \end{array}$	Neoprene
17.	$\begin{array}{c} \text{COOH} \\   \\ \text{C}_6\text{H}_4 \\   \\ \text{COOH} \end{array} + \text{HO}-\text{CH}_2-\text{CH}_2-\text{OH}$	$\begin{array}{c} \text{O} \quad \quad \text{O} \\    \quad \quad    \\ -\text{C}-\text{C}_6\text{H}_4-\text{C}-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}- \end{array}$	Poly(ethylene terephthalate, Terylene, Dacron or Mylar

18.			Kodel Polyester
19.			Polyethylene phthalate alkyd resin (Glyptal)
20.	 <p>Caprolactam</p>		Nylon-6
21.	<p> <math>\text{NH}_2(\text{CH}_2)_6\text{NH}_2</math>            Hexamethylenediamine            +  <math>\text{HO}-\text{C}(=\text{O})-(\text{CH}_2)_4-\text{C}(=\text{O})-\text{OH}</math>            Adipic Acid         </p>		Nylon - 66
22.	<p> <math>\text{NH}_2-\text{C}_6\text{H}_4-\text{NH}_2</math>            1,4-Diaminobenzene            +  <math>\text{Cl}-\text{C}(=\text{O})-\text{C}_6\text{H}_4-\text{C}(=\text{O})-\text{Cl}</math>            Terephthaloyl chloride         </p>		Kelvar
23.		—	Bakelite or resol
24.	<p> <math>\text{NH}_2-\text{C}(=\text{O})-\text{NH}_2</math> + HCHO            Urea         </p>	—	Urea- formaldehyde resin
25.	<p>            + HCHO            Melamine         </p>	—	Melamine- formaldehyde resin

## PRACTICAL ORGANIC CHEMISTRY

### Functional group analysis

**1. Unsaturation : Alkenes & alkynes:**

- (a) Bayers test : Cold dil alk.  $\text{KMnO}_4$  decolourisation test  
Purple colour  $\rightarrow$  Colourless +  $\text{MnO}_2$  (Brown ppt)
- (b)  $\text{Br}_2$  water decolourisation test  
Violet colourless of  $\text{Br}_2 \rightarrow$  Colourless

**2. Terminal alkynes:**

Confirmed by ppt of Acetylde ion with  $\text{NaNH}_2$  or  $\text{AgNO}_3$  or  $\text{Cu}_2\text{Cl}_2\text{NH}_4\text{OH}$

**3. Alkyl halides:**

- (a) If they are capable of carbocation formation then they will give ppt with  $\text{AgNO}_3$ .
- (b) Beilstein's test : A green colour is imported to the flame if small amount of organic compound is taken on copper wire.

**4. Alcohol:**

- (a) Cerric ammonium nitrate  $\rightarrow$  Give red colour
- (b) Boil with acetic acid & conc.  $\text{H}_2\text{SO}_4 \rightarrow$  fruity smell
- (c) 2-alkanol & ethanol also give Iodoform test  $\rightarrow$  Yellow ppt. of  $\text{CH}_3\text{I}$  on reaction with  $\text{I}_2 + \text{OH}$

**5. Aldehyde & Ketones:**

2,4- Dinitrophenyl hydrazide (or) Braddy's reagent give yellow, orange or red color with ald. & Ketones

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**6. Aldehydes:**

- (a) Tollen's test  $\rightarrow$  Silver mirror
- (b) Fehling's test {except benzaldehyde}  $\rightarrow$  Red colour
- (c) Benedicts test  $\rightarrow$  Red colour
- (d) Schiff's dye colour regeneration test  $\rightarrow$  Pink colour
- (e) Gly ppt with  $\text{HgCl}_2$ .

**7. Ketones:**

- (a) Methyl Ketones give haloform test
- (b)  $\alpha$ -hydroxy Ketones give Tollen's & Fehling test's too.

**8. Carboxylic acids:**

- (a) Brisk effervescence with aq.  $\text{NaHCO}_3$  solution.
- (b)  $\text{HCOOH}$  alone gives silver mirror test with Tollen's reagent.
- (c) Blue litmus  $\rightarrow$  red
- (d) Give fruity smell on reaction with alcohols.

**9. Phenols:**

- (a) Violet colouration with neutral  $\text{FeCl}_3$
- (b) Liebermann test
- (c) White ppt with  $\text{Br}_2$  water
- (d) Brisk effervescence with aq.  $\text{NaHCO}_3$  is observed in case of Nitrophenols.

**10. Primary amines:**

- (a) Carbylamine reaction  $\rightarrow$  Isonitriles have very distinctive foul odors
- (b) Hoffmann mustard oil reaction  $\rightarrow$  Oily liquid with mustard like smell.

11. Aromatic 1° amine  $\rightarrow$  diazo test

12. Amide boil with NaOH  $\rightarrow$  NH<sub>3</sub>

13. Nitrobenzene  $\rightarrow$  Mulliken Baker test  $\rightarrow$  Treat it with ZnNH<sub>4</sub>Cl then boil with Tollen's reagent  $\rightarrow$  Silver mirror will appear

**14. Proteins:**

- (a) **Biuret test** : Also used for urea  $\rightarrow$  Alkaline solution of protein treated with a drop of aq CuSO<sub>4</sub> when bluish violet colour is obtained
- (b) **Ninhydrin test** : Protein treated with a puridine solution of ninhydrin give colour ranging from deep blue to violet pink.

**DIFFERENTIATION TEST****D1. 1°, 2° & 3° alcohols :**

- (a) Luca's test : Lucas reagent is conc. HCl + ZnCl<sub>2</sub>
- (b) Victor Meyer's test (RBC test)
  - (i) 1° Alcohol  $\rightarrow$  Blood red colour

**DIFFERENTIATION TEST****D1. 1°, 2° & 3° alcohols :**

- (a) Luca's test : Lucas reagent is conc. HCl + ZnCl<sub>2</sub>
- (b) Victor Meyer's test (RBC test)
  - (i) 1° Alcohol  $\rightarrow$  Blood red colour
  - (ii) 2° Alcohol  $\rightarrow$  Blue
  - (iii) 3° Alcohol  $\rightarrow$  Colourless

**D2. 1°, 2° & 3° amines:**

- (a) Hinsberg's reagent
  - (i) 1° Amine yield a clear solution from which upon acidification an insoluble material separated.
  - (ii) 2° Amine yield an insoluble compound which is unaffected by acid
  - (iii) 3° Amine yield insoluble compound
- (b) Reaction with HNO<sub>2</sub>